Electronic Supplementary Information

Calix[4]arene nitroxide tetraradical and octaradical

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1. Complete reference 19.

19. (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*, Revision E.01 (Gaussian, Wallingford, CT, 2004). (b) Gaussian 09, Revision **A.1**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J.

Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

2. General procedures and materials, including NMR spectroscopy.

Throughout the following paragraphs labels "AO-3-77" and alike correspond to sample or experiment codes directly traceable to the laboratory notebooks or raw data.

Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone. Palladium catalyst, $Pd[P(t\text{-}Bu)_3]_2$, was obtained from Streck Laboratories, and stored in a freezer inside Vacuum Atmospheres glovebox. Per-deuterated solvents for NMR spectroscopy were obtained from Cambridge Isotope Laboratories. *t*-BuLi (pentane) was obtained from Aldrich; prior to use, the concentration was determined by titration with *N*-pivaloyl-*o*-toluidine.[S1] All other commercially available chemicals were obtained from either Aldrich or Acros, unless indicated otherwise. Column chromatography (0–20 psig pressure) and thin layer chromatography was carried out on silica gel. Standard techniques for synthesis under inert atmosphere, using Schlenk glassware and gloveboxes (Vacuum Atmospheres), were employed.

NMR spectra were obtained with a Bruker spectrometer (^{1}H, 400 MHz, 500 MHz and 600 mHz) using chloroform-*d* ($CDCl_3$) and acetone-d_6 as solvent; the 500 MHz instrument was equipped with a cryoprobe. The chemical shift references were as follows: (^{1}H) chloroform-*d*, 7.26 ppm; (^{13}C) chloroform-*d*, 77.00 ppm (chloroform-*d*), (^{1}H) acetone-d_5, 2.05 ppm; (^{13}C) acetone-d_5, 29.92 ppm (acetone-d_6). Typical 1D FID was subjected to exponential multiplication with a line broadening exponent (LB) of 0.3 Hz (for ^{1}H) and 1.0 – 2.0 Hz (for ^{13}C). For selected spectra, smaller (or negative) values of LB and additional Gaussian multiplication (GB) were used, to resolve closely spaced resonances, as indicated in the spectral data summaries.

Paramagnetic ^{1}H NMR spectra were obtained on concentrated solutions of **2** and **3** in chloroform-*d*, using 3-mm samples tube and 500 MHz NMR instrument with a cryoprobe. The employed concentrations were limited by the available amounts of **2** and **3** and their solubility. Examples of ^{1}H NMR spectra for specific samples of **2** and **3** are presented in section 8.

The protons of the aryl moieties directly attached to nitroxides are not detected because of too broad lines (and large positive or negative chemical shifts), as expected for large values of $|A(^1\text{H})|$ predicted by computations. All other protons in **2a** and **3a** with relatively smaller values of $|A(^1\text{H})|$ are detectable in **2** and **3** as broadened peaks. The chemical shifts of these resonances, labeled as "**a**", "**b**", "**c**", and "**d**" (Fig. 2, main text) are shifted from their corresponding values in diamagnetic hydroxylamines by the paramagnetic shifts (not corrected for bulk magnetic susceptibility) that are in qualitative agreement with the calculated magnitudes and signs of scaled $A(^1\text{H})$ in **2a** and **3a**. Computed values of $A(^1\text{H})$ (unscaled) are presented in Fig. S16, Section 6. In addition, the paramagnetic shifts for protons of the calix[4]arene macrocycle (resonances labeled as "**c**" and "**d**") have opposite signs in **2** and **3** (Fig. 2, main text), due to *para* vs. *meta* connectivity of the nitroxides to the scaffold. Specifically, paramagnetic shifts for resonances labeled **d** (Fig. 2, main text), assigned to the CH_2-groups of the calix[4]arene macrocycles, are –9.0 and +8.4 ppm in **2** and **3**.

IR spectra were obtained using a Nicolet Avatar 360 FT-IR instrument, equipped with an ATR sampling accessory (Spectra Tech, Inc.). A few drops of the compound in CH_2Cl_2 were applied to the surface of a ZnSe ATR plate horizontal parallelogram (45°, Wilmad). After the solvent evaporated, the spectrum was acquired (2-cm^{-1} resolution).

FAB MS analyses were carried out in 3-nitrobenzyl alcohol (3-NBA) or *o*-nitrophenyl octyl ether (ONPOE) matrices at the Nebraska Center for Mass Spectrometry.

3. CW EPR spectroscopy.

CW X-band EPR spectra for tetraradicals **2** and **2b**, and octaradical **3** were acquired on a Bruker EMX instrument, equipped with a frequency counter and dual mode cavity. Temperature was controlled with nitrogen flow system (130–300 K). The samples were contained in either 4-mm EPR quartz tubes or 5-mm SQUID sample tubes. All spectra were obtained with the oscillating magnetic field perpendicular (TE_{102}) to the swept magnetic field. The *g*-values were referenced using DPPH (g = 2.0037, powder, Aldrich).

Rigid lattice (133 K) CW EPR spectra of tetraradical **2** at a series of concentrations in 2-MeTHF (0.03 to 1.0 mM) are shown in Figures S1A, B, C, and S2. Two dominant spectral features may be identified: dipolar split side bands with $2D_{\perp} \sim 72$ mT that are characteristic of $S = 1$ (conformation $\mathbf{2_b}$) and a sharp band in the center of the spectrum with $\Delta B_{pp} \sim 1.5$ mT (conformation $\mathbf{2_s}$). If the point dipole approximation is used, the dipolar splitting for $\mathbf{2_b}$ corresponds to an interspin distance of 4.3 Å. This distance is in good agreement with the values obtained by DFT calculations (Table S4, Section 6). The observation of a $|\Delta m_s| = 2$ (half-field transition) is consistent with strong dipolar interactions. There is no evidence of concentration dependence of the relative intensities of the two spectral features; therefore, neither $\mathbf{2_b}$ nor $\mathbf{2_s}$ is attributed to aggregation. Consequently, $\mathbf{2_b}$ and $\mathbf{2_s}$ are attributed to different conformations of tetraradical **2**. Both spectral features also are present in 2-MeTHF/MeOH (2:1) (Fig. S4B) and in toluene/$CHCl_3$ (4:1) (Fig. S5B). Double integration of the spectra indicates that the sharp center band ($\mathbf{2_s}$) accounts for about 30% of the spins in 2-MeTHF, but only about 10% in 2-MeTHF/MeOH (2:1). The fluid solution spectra of **2** are very broad (Fig. S3, S4A, S5A), which is consistent with incomplete motional averaging of the anisotropy observed in the rigid lattice. The observation of only one signal implies rapid averaging of the conformations that give the

dipolar split and relatively sharp signals in the immobilized samples. The poorly resolved nitrogen hyperfine splitting is about 0.7 mT, which is half the hyperfine splitting for the corresponding monoradicals, and indicates that there is significant exchange interaction between pairs of nitroxyls. Values of J that are large enough to average hyperfine splittings to two nitrogens may still be 'weak' by magnetic susceptibility standards.

The spectrum of $\mathbf{2_b}$ is similar, but with somewhat larger dipolar splitting, compared to rigid-lattice spectra observed for 1,3-diradical derivatives of calixarenes.[S2] The dipolar splitting is therefore attributed to through-space pairwise interactions in the tetraradical accompanied by very weak through-bond interaction between the two pairs. The spin system for $\mathbf{2_b}$ thus behaves as two essentially independent diradicals. The narrow spectrum of $\mathbf{2_s}$ is similar to that of tetraradical **1** in which the symmetry was high enough and exchange narrowing sufficiently effective that dipolar splittings were not observed.[S2]

Tetraradical **2b** has R = HEG instead of the smaller R group in **2**. The rigid lattice (133 K) CW spectrum of **2b** in 2-MeTHF (Fig. S6) exhibits only a sharp signal with ΔB_{pp} = 1.5 mT, similar to component $\mathbf{2_s}$ in the spectra of **2**. The absence of a detectable $|\Delta m_s| = 2$ transition indicates much weaker electron-electron dipolar interaction, consistent with the absence of resolved dipolar splitting in the $|\Delta m_s| = 1$ signal. In fluid solution, the spectrum of **2b** is much sharper than the spectrum of **2**, consistent with efficient motional averaging of relatively small anisotropy (Fig. S8). The fluid solution spectrum is split into 5 lines due to equivalent interaction with 2 nitrogens. The unequal linewidths (sometimes called alternating linewidths) are characteristic of a system in which dynamic averaging of hyperfine interaction is occurring on the EPR timescale. In ethanol at 133 K, dipolar split side bands are also observed for **2b** (Fig. S7). It is therefore proposed that the change in the R groups has shifted the conformational

equilibrium to favor the conformation with resolved dipolar coupling, in analogy to conformation $\mathbf{2_b}$ in **2**.

The rigid lattice (133 K) CW spectrum of octaradical **3** in MeTHF (Fig. S9) has a narrow central band and broad side bands attributed to dipolar splittings of about 10 and 20 mT. The spectrum is analyzed by analogy with that of **2**. The central line is attributed to conformation $\mathbf{3_s}$ and the dipolar split side bands are attributed to a second conformation $\mathbf{3_b}$. The observation of a relatively weak $|\Delta m_s| = 2$ transition is consistent with a modest population of the conformation with resolved dipolar coupling. The dipolar splittings for $\mathbf{3_b}$ are somewhat smaller than observed for the *m*-phenylene diradicals ($D \sim 12$ to 17 mT, depending on solvent).[S3] Qualitatively, the magnitude of the dipolar splittings in $\mathbf{3_b}$ can be viewed as follows. The principle axes for the dipolar interactions in the *m*-phenylene diradicals are approximately perpendicular to the principle axes for the through-space dipolar interaction between cofacial pairs of diradicals. Since the dipolar coupling along the principle axis and in the perpendicular plane have opposite signs, these two dipolar interactions partially cancel, resulting in a relatively small net dipolar coupling for the pair of interacting diradicals. The pulse turning angle measurements described in section 4 suggest that the sharp signal in the center of the spectrum has *S* intermediate between 1 and 2, or a superposition of transitions.

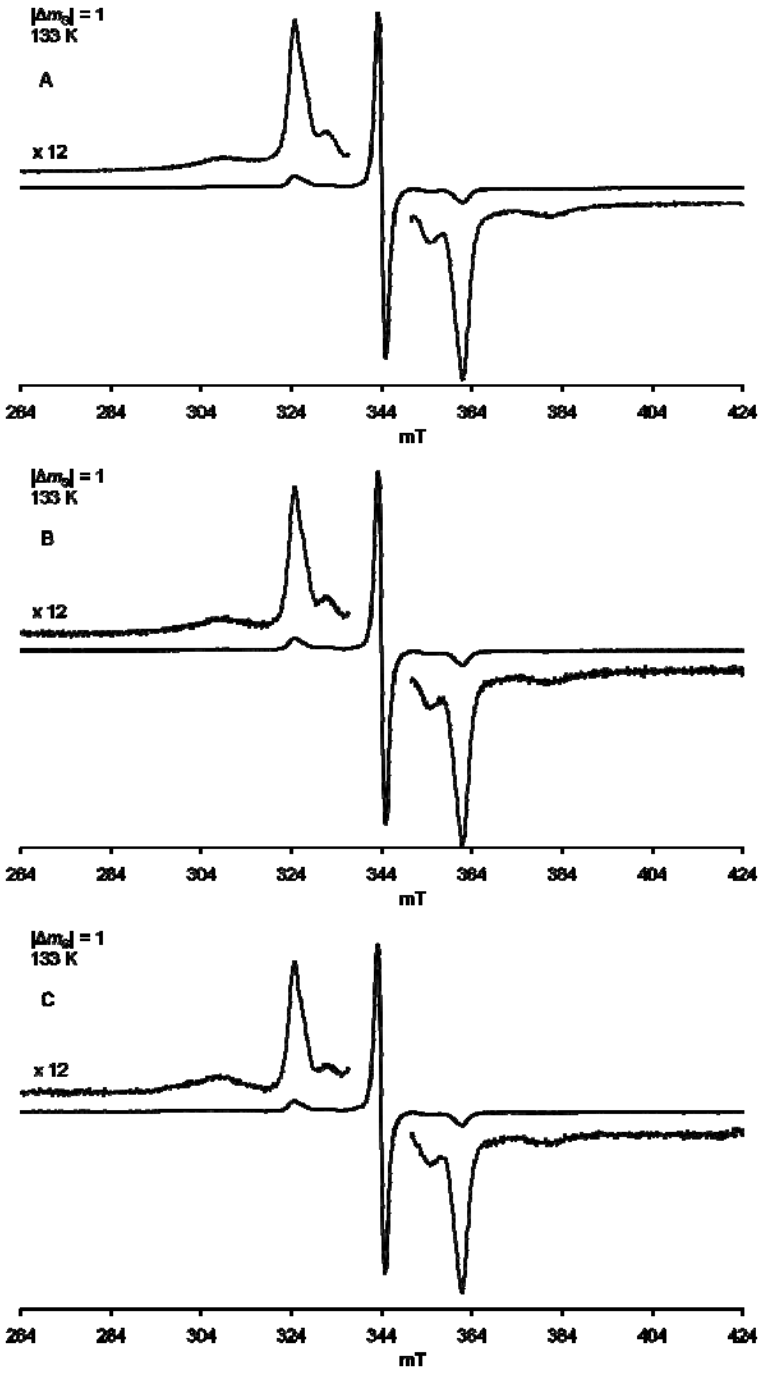


Figure S1. CW EPR spectra ($|\Delta m_s| = 1$) calix[4]arene nitroxide tetraradical **2** in 2-MeTHF at 133 K (4-mm tube, sample label: AO433col1&2). **(A) Conc. 0.25 mM**; X-Band, ν = 9.6542 GHz, EPR label: AO586r6 (SW1600, 10dB, 5G). **(B) Conc. 0.06 mM**; X-Band, ν = 9.6528 GHz, 4-mm tube, EPR label: AO586r9 (SW1600, 10dB, 5G). **(C) Conc. 0.03 mM**; X-Band, ν = 9.6499 GHz, 4-mm tube, EPR label: AO586r11 (SW1600, 10dB, 5G).

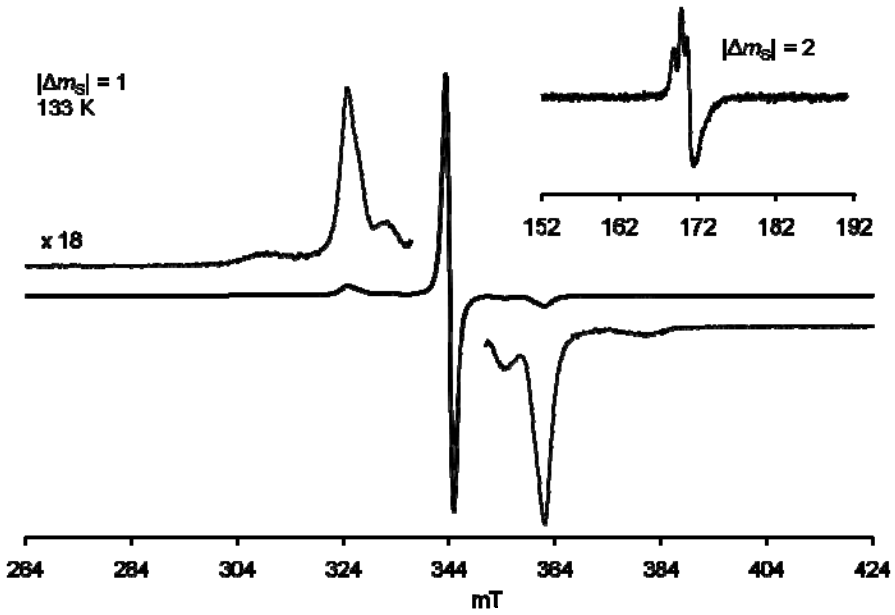


Figure S2. CW EPR (X-Band, ν = 9.6531 GHz, $|\Delta m_s| = 1$) spectrum of 1 mM calix[4]arene nitroxide tetraradical **2** in 2-MeTHF at 133 K, 4-mm tube, sample label: AO420colfr2−3, EPR label: AO434r16/r12, SW1600, 20dB, 3G. Inset plot: $|\Delta m_s| = 2$ region, ν = 9.6529 GHz (SW400, 10dB, 4G).

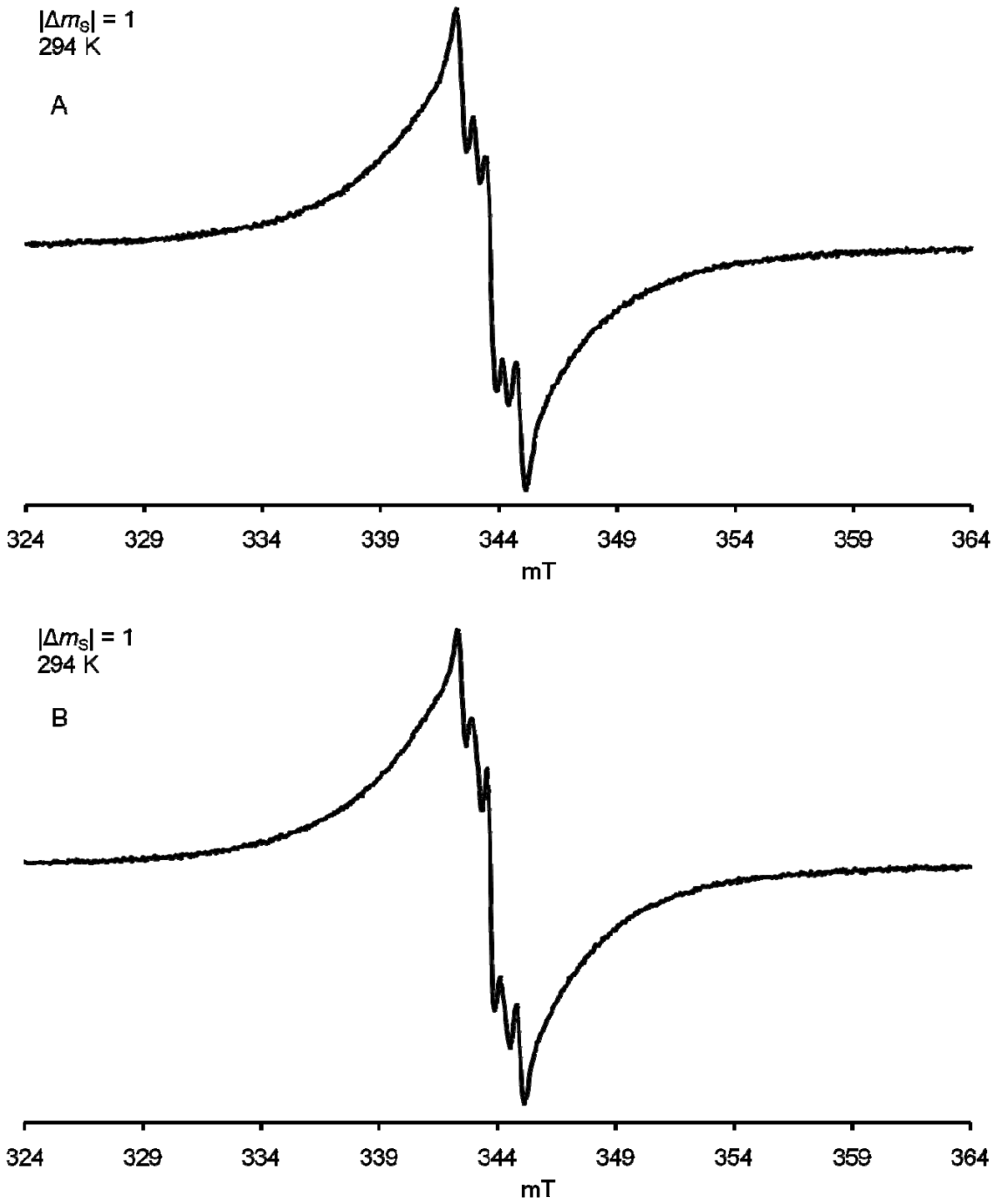


Figure S3. CW EPR spectra ($|\Delta m_s| = 1$) of calix[4]arene nitroxide tetraradical **2** in 2-MeTHF at 294 K. **(A) Conc. 1 mM**; X-Band, ν = 9.6469 GHz, 4-mm tube, sample label: AO420colfr2-3, EPR label: AO434r2, SW400, 20dB, 2G. **(B) Conc. 0.25 mM**; X-Band, ν = 9.6481 GHz, 4-mm tube, sample label: AO433col1&2, EPR label: AO563r5, SW400, 15dB, 2G.

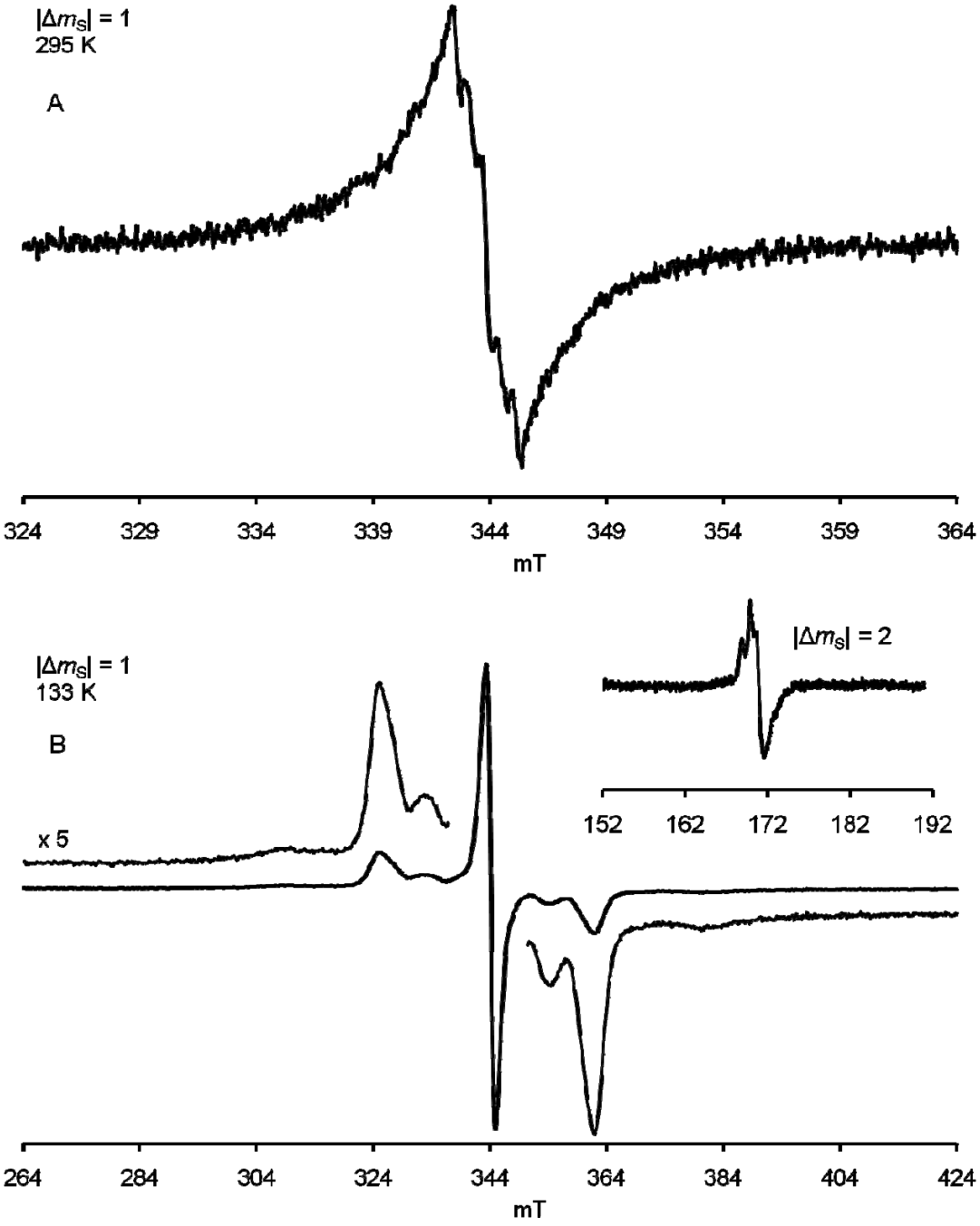


Figure S4. CW EPR spectra of 0.17 mM calix[4]arene nitroxide tetraradical **2** in 2-MeTHF/MeOH, 2:1 (sample label: AO433col1&2). **(A) $|\Delta m_s| = 1$ at 295 K**; X-Band, ν = 9.6513 GHz, 4-mm tube, EPR label: AO563r9, SW400, 20dB, 5G). **(B) $|\Delta m_s| = 1$ at 133 K**; X-Band, ν = 9.6533 GHz, 4-mm tube, EPR label: AO563r11, SW1600, 10dB, 3G; inset plot: $|\Delta m_s| = 2$ region, ν = 9.6533 GHz (SW400, 10dB, 5G).

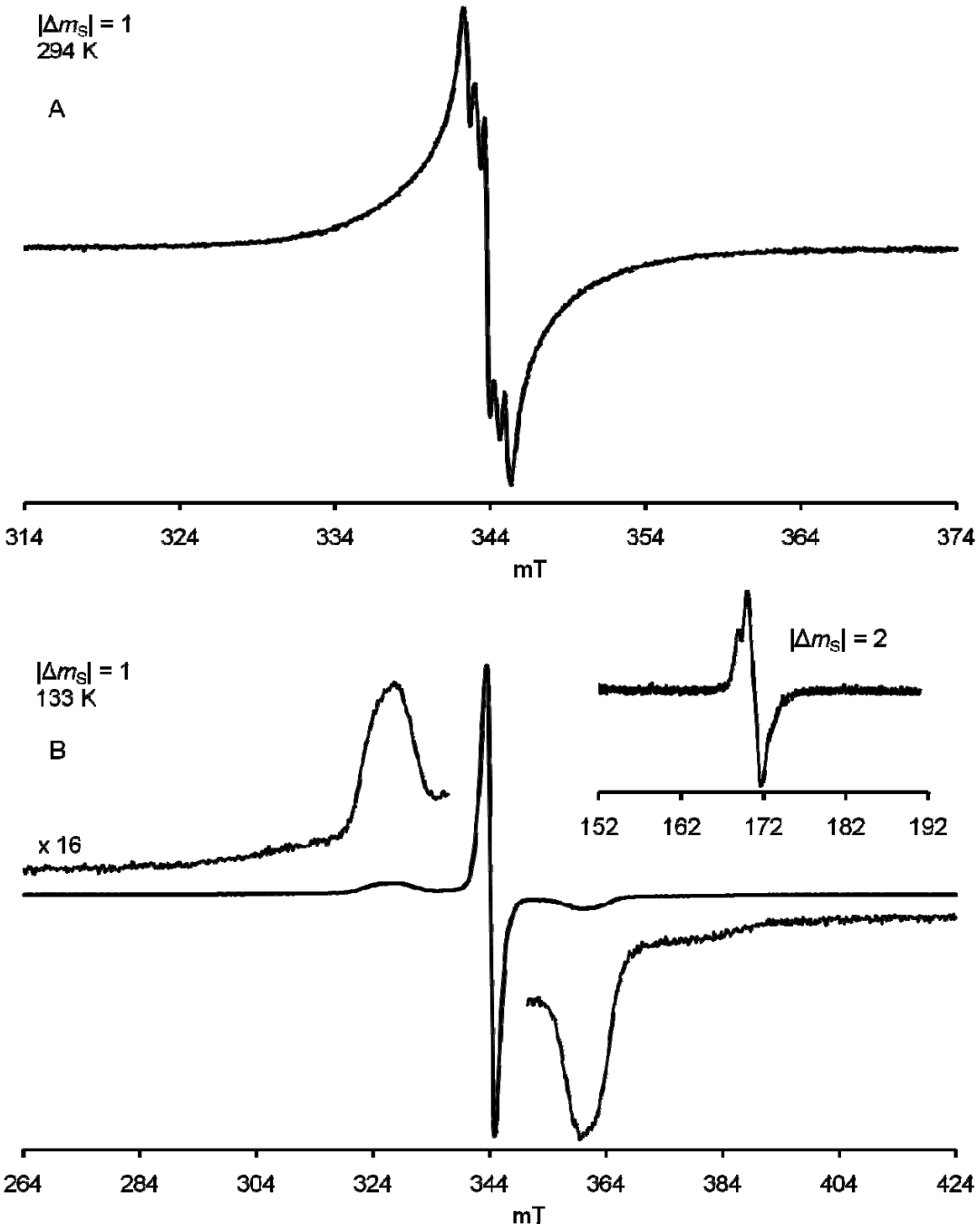


Figure S5. CW EPR spectra of 0.2 mM calix[4]arene nitroxide tetraradical **2** in toluene/$CHCl_3$, 4:1 (sample label: AO433col1&2). **(A) $|\Delta m_s| = 1$ at 294 K**; X-Band, ν = 9.6488 GHz, 4-mm tube, EPR label: AO564r21, SW600, 20dB, 2G. **(B) $|\Delta m_s| = 1$ at 133 K**; X-Band, ν = 9.6557 GHz, 4-mm tube, EPR label: AO564r25, SW1600, 20dB, 3G; inset plot: $|\Delta m_s| = 2$ region, ν = 9.6556 GHz (SW400, 10dB, 4G).

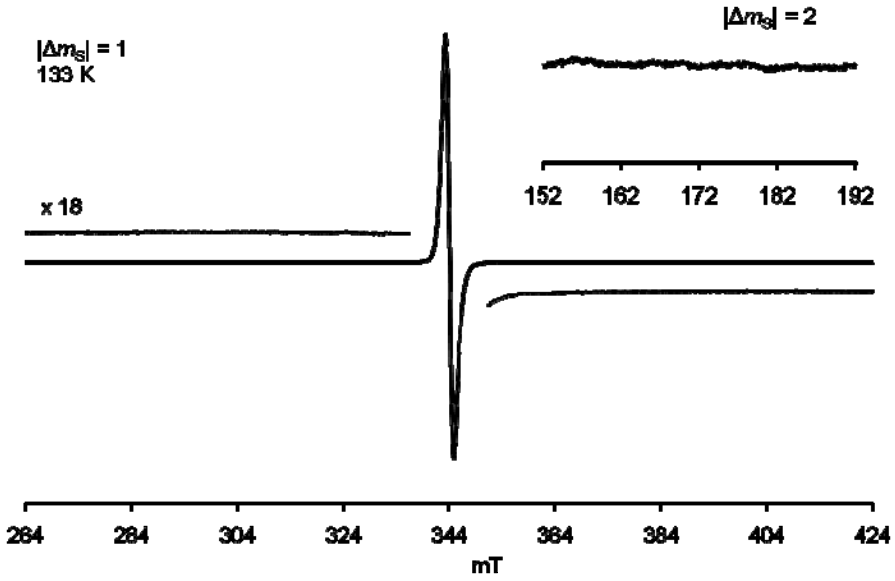


Figure S6. CW EPR (X-Band, ν = 9.6534 GHz, $|\Delta m_s| = 1$) spectrum of 1 mM calix[4]arene nitroxide tetraradical **2b** (R = HEG) in 2-MeTHF at 133 K, 4-mm tube, sample label: AO480col, EPR label: AO587r2/r4, SW1600, 20dB, 5G. Inset plot: $|\Delta m_s| = 2$ region, ν = 9.6517 GHz (SW400, 10dB, 5G).

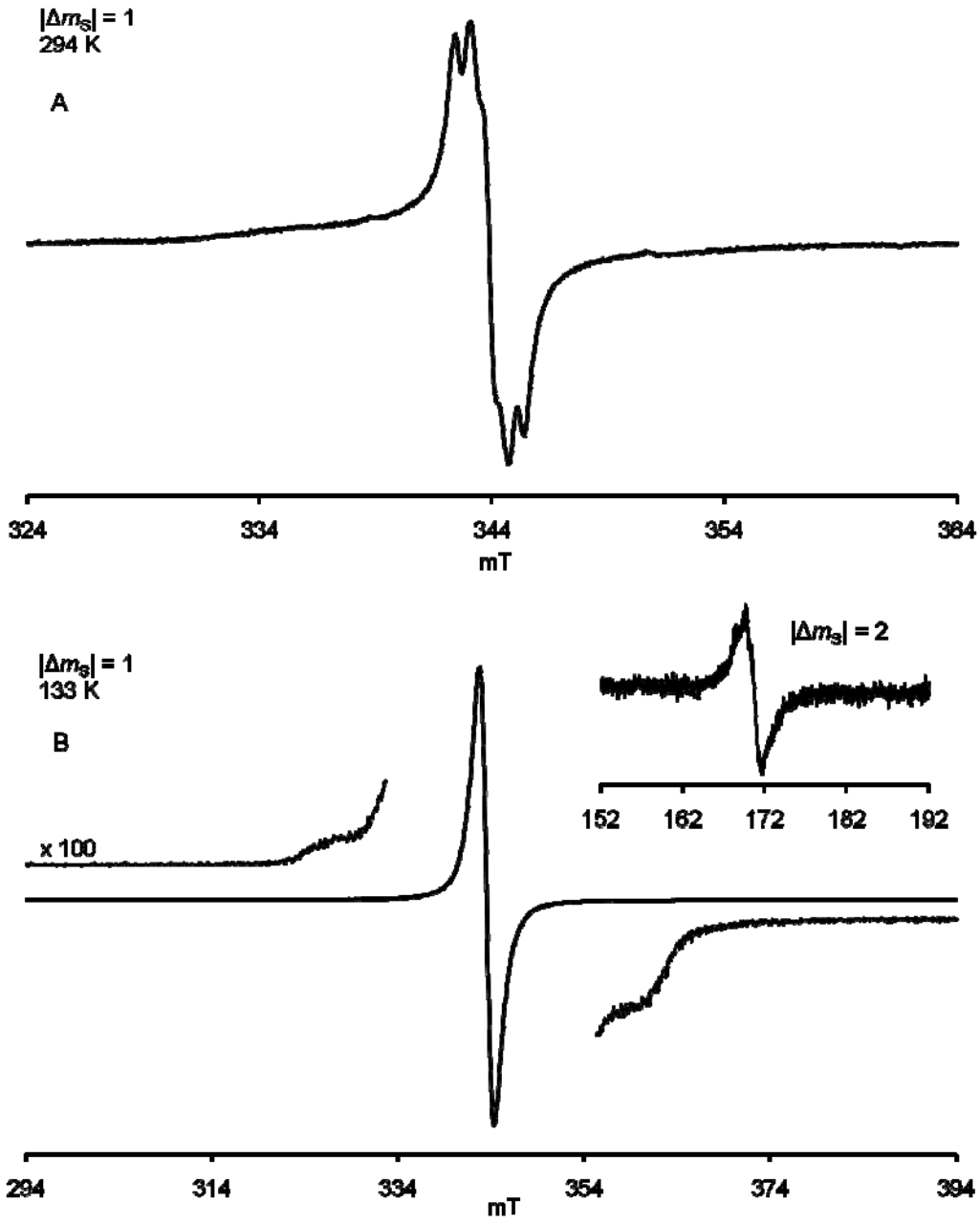


Figure S7. CW EPR spectra of 1 mM calix[4]arene nitroxide tetraradical **2b** (R = HEG) in EtOH (sample label: AO480col). **(A) $|\Delta m_s| = 1$ at 294 K;** X-Band, ν = 9.6521 GHz, 4-mm tube, EPR label: AO545r7, SW400, 10dB, 4G. **(B) $|\Delta m_s| = 1$ at 133 K;** X-Band, ν = 9.6419 GHz, 4-mm tube, EPR label: AO545r5, SW1000, 20dB, 4G; inset plot: $|\Delta m_s| = 2$ region, ν = 9.6419 GHz, SW400, 5dB, 4G.

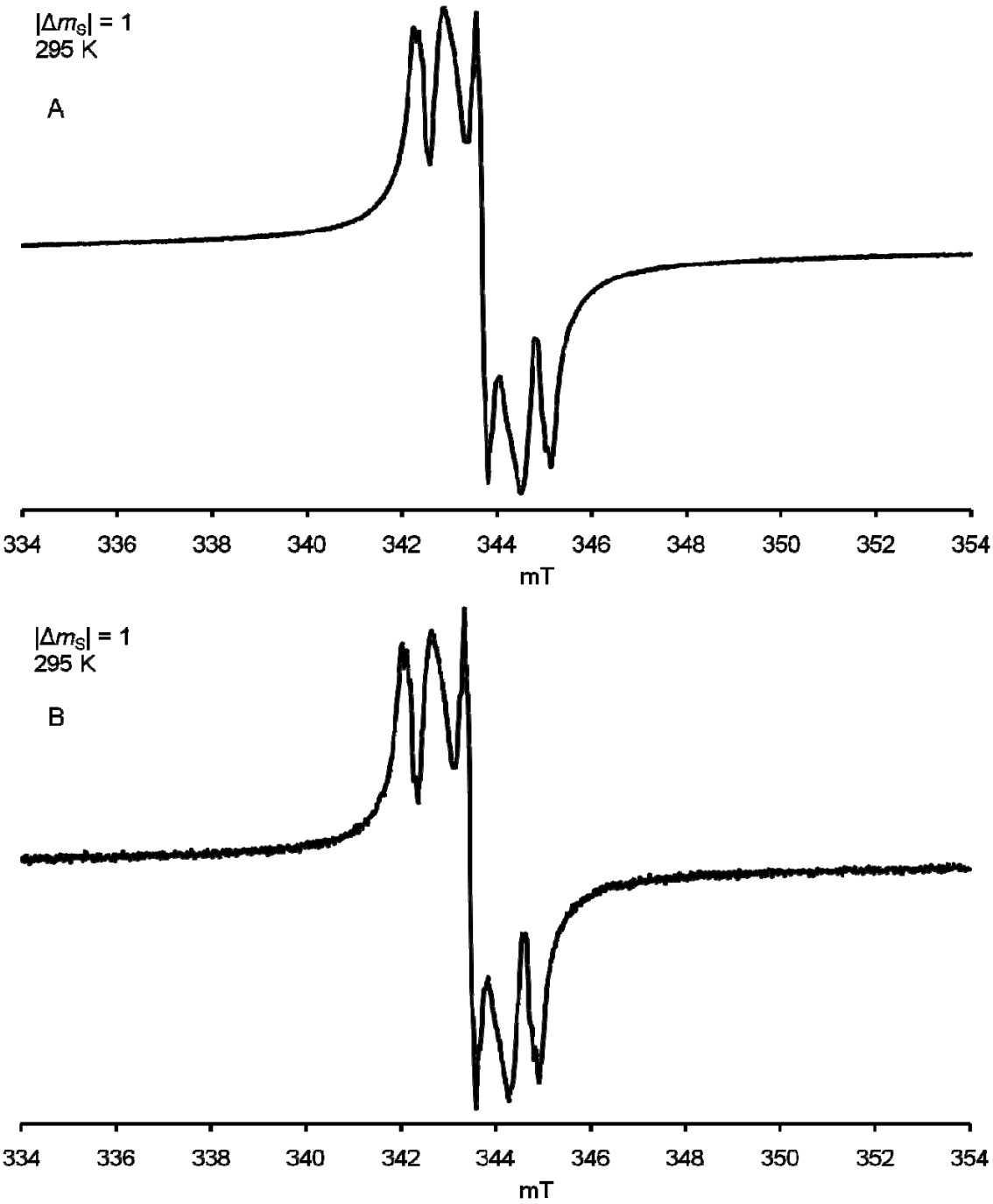


Figure S8. CW EPR spectra ($|\Delta m_s| = 1$) of calix[4]arene nitroxide tetraradical **2b** (R = HEG) in 2-MeTHF at 295 K. **(A) Conc. 1 mM**; X-Band, ν = 9.6494 GHz, 4-mm tube, sample label: AO480col, EPR label: AO587r13, SW200, 10dB, 0.5G. **(B) Conc. 0.25 mM**; X-Band, ν = 9.6433 GHz, 4-mm tube, sample label: AO480col, EPR label: AO587r23, SW200, 10 dB, 0.5G.

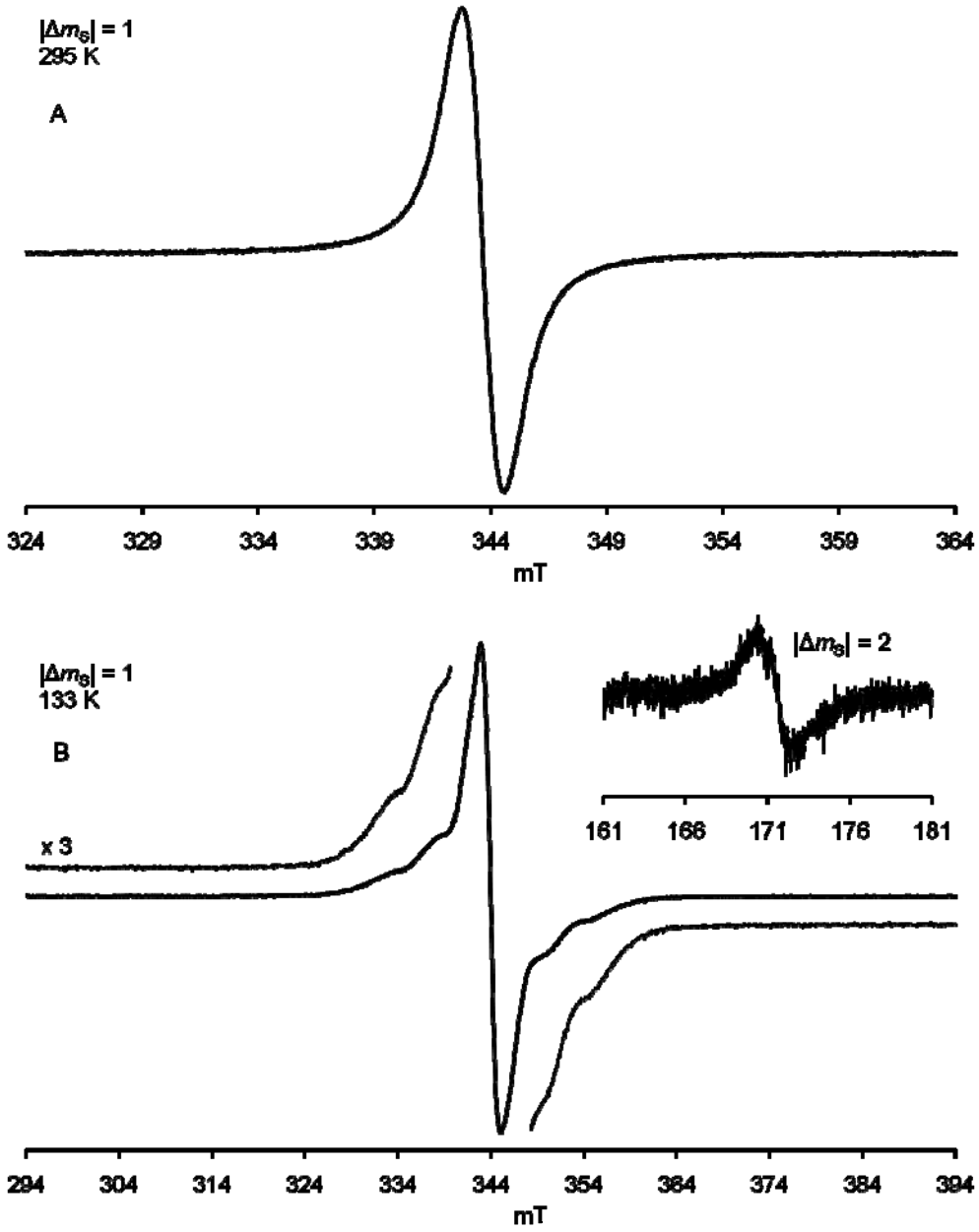


Figure S9. CW EPR spectra of 1 mM calix[4]arene nitroxide octaradical **3** in 2-MeTHF (sample label: AO437col). **(A) $|\Delta m_s| = 1$ at 295 K**; X-Band, ν = 9.6478 GHz, 4-mm tube, EPR label: AO556r1, SW400, 30dB, 1G. **(B) $|\Delta m_s| = 1$ at 133 K**; X-Band, ν = 9.6554 GHz, 4-mm tube, EPR label: AO556r2, SW1000, 30dB, 1G; inset plot: $|\Delta m_s| = 2$ region, ν = 9.6504 GHz (SW200, 10dB, 5G).

4. Pulsed EPR spectroscopy.

Prior studies of **1** were performed in toluene/$CHCl_3$ (4:1).[S2] However **2** and **3** have low solubility in this solvent and tend to precipitate at low temperatures. To obtain adequate solubility over the full range of temperatures and permit comparison without corrections for solvent effects, all pulsed EPR experiments for **1**, **2**, and **3** that are reported in this work were performed in 2-MeTHF/MeOH (2:1).

Spectroscopy:

Electron spin lattice relaxation rates were measured by saturation recovery (SR) on a locally built spectrometer[S4] or on a Bruker E580. For comparison, relaxation rates at a few temperatures were also measured by inversion recovery, and the relaxation rates obtained by the two methods were in good agreement. Relaxation rates as a function of temperature were measured at the magnetic field position that corresponds to the maximum intensity in the absorption spectrum. The observe power was reduced until further decrease had no impact on apparent T_1. In order to minimize contributions from spectral diffusion to the recovery signal, the pump pulse was longer than T_1. For **2** and **3** a single exponential give a good fit. Data for **1** fit well with the sum of two exponentials. For **1** the component with larger amplitude was used in the analysis of the temperature dependence; both components have similar temperature dependence.

Electron spin dephasing rates were measured with a 90^o-τ-180^o-τ-echo pulse sequence on a Bruker E580 spectrometer. The Q of the over coupled resonator, measured by pulse ringdown, was about 150. The attenuation was adjusted to maximize the intensity of the two pulse echo. Relaxation rates as a function of temperature were measured at the position of maximum echo intensity in the field-swept spectrum.

The spin flip angle for the transition between m_S and m_S+1 for spin state S is given in eq. 1.[S5,S6]

$$\theta = c\gamma B_1 t_p \quad \text{and} \quad c = [S(S+1)-m_S(m_S+1)]^{1/2}, \qquad (1)$$

where θ is the turning angle, t_p is the pulse length, and B_1 is the microwave magnetic field at the resonator.

The B_1 is related to the incident power, as shown in eq. (2).

$$B_1 = \alpha(Q_L P)^{1/2} \qquad (2)$$

where α is determined by the resonator efficiency, Q_L is the loaded Q of the resonator and P is power incident on the resonator in watts.

Experimentally, the power attenuation was adjusted to give a 90° pulse for a particular transition. Since it is known that $S = ½$ for a monoradical, the value of c for other spin states can be found from the ratio of $(QP)^{1/2}$ for the unknown spin state to that for a known $S = ½$ system. The resulting values of c for radicals **1**, the conformations of **2** and **3** with small D (**2**$_s$ and **3**$_s$) are shown in Table S1.

Table S1. Attenuation for 90° turning angle for the radicals.

Radical	Resonator Q	Attenuation (dB)[a]	c (eq. 1)
Monoradical	119	17	1.0[b]
1 (tetraradical)	118	22.5	1.9
2$_s$ (tetraradical)[c]	123, 119	21.0	1.6
3$_s$ (octaradical)	128	23.5	2.0

[a] The accuracy of the attenuation setting is about 0.5 dB, which corresponds to an uncertainty of about ±0.1 in c. [b] By definition c = 1 for $S = ½$. [c] The measurements was performed in the center of the spectrum where the conformation with small D dominates.

These experiments were performed at the position of maximum echo intensity in the field-swept spectra. The $S = 1$, c = 1.41 and for $S = 2$, c = 2.0 ($m_S = -2$) or 2.45 ($m_S = -1$). The values of c observed for **2** and **3** are greater than predicted for $S = 1$, which suggests that there may be overlapping transitions for conformations with $S = 1$ and $S = 2$.

Field-swept echo-detected EPR spectra

The field-swept echo-detected spectrum of tetraradical **2** at 40 K (Figure S10) has two components. The sharp signal in the center is characteristic of relatively small D and the underlying broad signal is characteristic of much larger D. This spectrum is consistent with integration of the CW spectra shown in Figure S4. The broad component has $D_\perp$ about 35 mT which corresponds to a point dipole distance of about 4.3 Å for $S = 1$. The field-swept echo-detected spectrum of octaradical **3** is shown in Figure S11. The relatively narrow spectral width is consistent with integration of the CW spectrum shown in Figure S9.

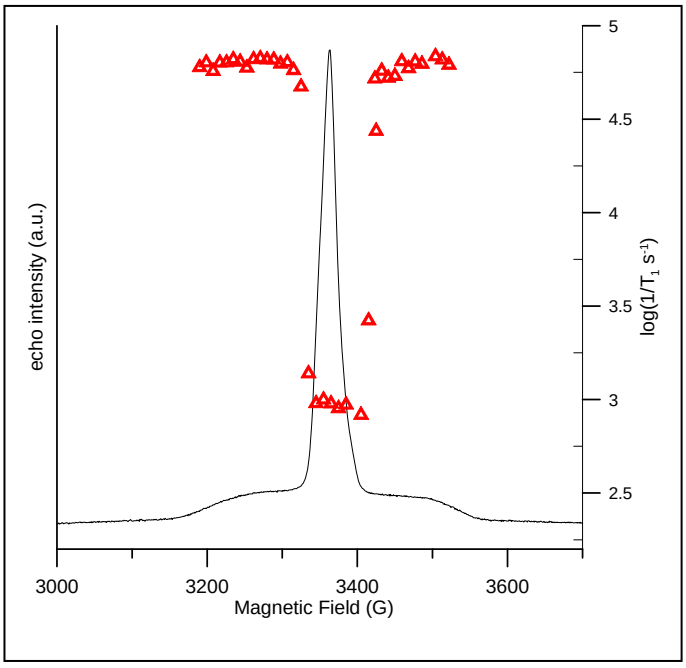


Figure S10. Field-swept echo-detected spectrum of **2** in 2-MeTHF/MeOH (2:1), and dependence of $1/T_1$ (red triangles) on position in the spectrum at 40 K.

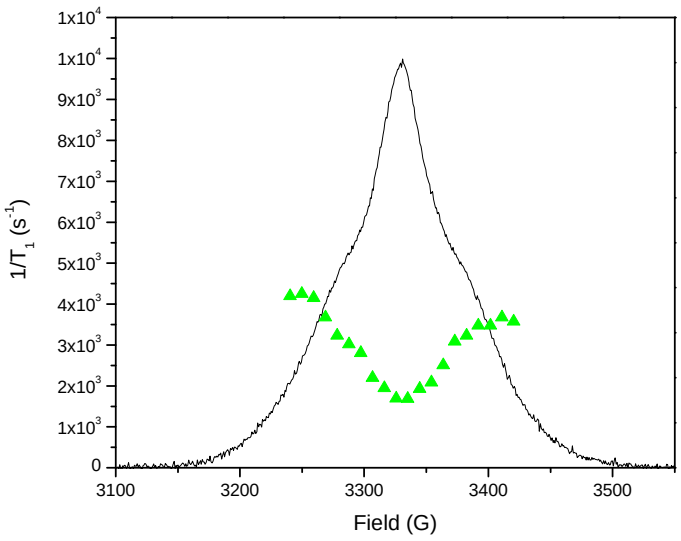


Figure S11. Field-swept echo-detected spectrum of **3** in 2-MeTHF/MeOH (2:1), and dependence of $1/T_1$ (▲) on position in the spectrum at 40 K.

For **2** at 40 K, the spin lattice relaxation rates are faster by about two orders of magnitude in the wings where the conformation with larger *D* (**2**$_\mathbf{b}$) dominates, than in the center of the spectrum where the conformation with smaller value of *D* (**2**$_\mathbf{s}$) dominates (Figure S10). This observation suggests that larger values of *D* result in faster spin-lattice relaxation. At 40 K, T_1 for the conformation of **2** with larger *D* (**2**$_\mathbf{b}$) is 16 μs, which is similar to that for **1** (16 μs), which has strong electron-electron coupling. At 40 K, the orientation dependence of $1/T_1$ for **3** (Figure S11) is only about a factor of 2. The smaller orientation dependence for **3** is attributed to the smaller value of *D* and the overlap of transitions.

Temperature dependence of T_m

Spin echo dephasing curves were fit with Eq. (3). Values of x were between 0.5 and 1.3, so to facilitate comparisons in Figure S12, x was fixed at 1.

$$Y(\tau) = Y_0 \exp(-(\frac{2\tau}{T_m})^x) \qquad (3)$$

At low temperatures, nitroxyl spin echo dephasing rates usually are dominated by nuclear spin diffusion, and decay curves in solvents that do not contain aliphatic methyls can be fit with x ~ 2.[S7] However, at 10 K the limiting values of x for **1**, **2**, and **3** are 1.3, 1.1, and 0.8, respectively. The value of x decreases with increasing temperature which indicates domination by dynamic processes. Rotation of aliphatic methyl groups in the solvent causes faster dephasing and values of x ~ 1. Values of x < 1, as was observed for **1**, **2**, and **3** in 2-MeTHF/MeOH (2:1), indicate a high concentration of methyls in the vicinity of the nitroxyl N-O. The limiting value of T_m for **1** at 10 K in 2-MeTHF/MeOH (2:1) was about 3 μs (Figure S12) which is somewhat shorter than the 3.5 μs that was observed for **1** in toluene/$CHCl_3$ (4:1).[S2]

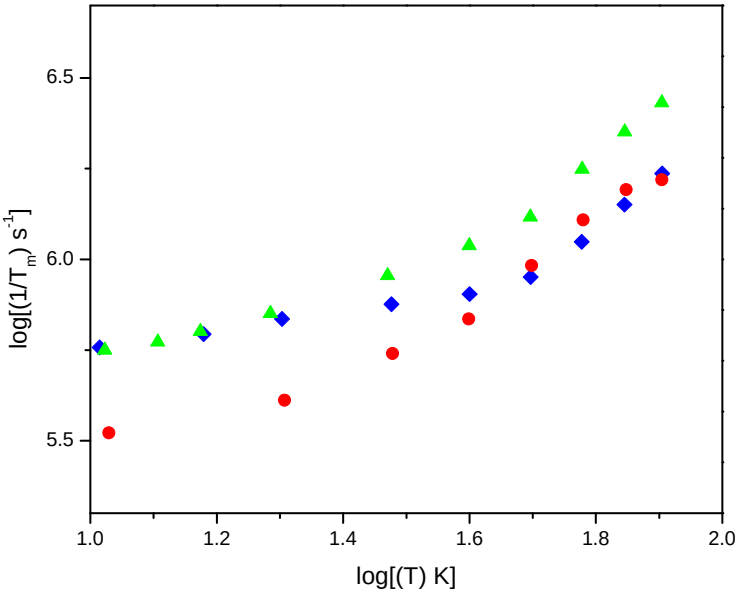


Figure S12. Temperature dependence of $1/T_m$ for **1** (●) and conformations of **2** (◆) and **3** (▲) with small *D* (**2**$_s$ and **3**$_s$) in 2-MeTHF/MeOH (2:1).

The limiting values of T_m for **2** and **3** at 10 K in 2-MeTHF/MeOH (2:1) were about 1.8 μs (Figure S12). It is proposed that the limiting values of T_m are shorter for **2** and **3** than for **1** because there are more solvent methyl groups in the immediate vicinity of the unpaired electrons

on the radical-containing side-chains of **2** and **3** that extend further from the calix[4]arene than in **1**.

For nitroxide monoradicals $1/T_m$ is approximately independent of temperature below about 80 K.[S7,S8] For nitroxide polyradicals **1**, **2**, and **3**, $1/T_m$ increases by about a factor of two between 10 and 40 K. At 40 K there is only about 10% variation in T_m for **3** (which has small *D*) as a function of position in the spectrum. In the wings of the signal for **2**, where the conformation with larger *D* (**2b**) dominates, $1/T_m$ at 40 K is more than twice as fast as in the center of the spectrum, which demonstrates the impact of *D* on dephasing rates. $1/T_m$ becomes more strongly temperature dependent above 40 K. The strong temperature dependence of $1/T_m$ above 40 K for **1**, **2**, and **3** is attributed to modulation of electron-electron spin interaction.[S8]

Temperature dependence of $1/T_1$

The temperature dependence of the spin lattice relaxation rates was modeled as the sum of contributions (Eq. 4)[S9,S10] from the direct process (Eq. 5) and the Raman process (Eq. 6). Since the glass transition temperature of 2-MeTHF/MeOH (2:1) is low (about 130 to 140 K), there is no temperature regime in which the characteristic temperature dependence of the local mode was observed.[S11] Therefore, a local mode was not included in the modeling of the temperature dependence of $1/T_1$.

$$\frac{1}{T_1} = \frac{1}{T_1^{Dir}} + \frac{1}{T_1^{Ram}} \tag{4}$$

Where $$\frac{1}{T_1^{Dir}} = C_{dir}(\alpha + T) \tag{5}$$

$$\frac{1}{T_1^{Ram}} = C_{Ram}\left(\frac{T}{\theta_D}\right)^9 J_8\left(\frac{\theta_D}{T}\right) \quad \text{where } J_8\left(\frac{\theta_D}{T}\right) = \int_0^{\frac{\theta_D}{T}} x^8 \frac{e^x}{(e^x - 1)^2} dx \tag{6}$$

C_{dir} and C_{Ram}, are adjustable parameters that scale the contributions from the corresponding process, θ_D is the Debye temperature in K, and α is a offset parameter.

The temperature dependence of $1/T_1$ for **2** and **3** were studied in the center of the spectrum, where the conformations with smaller *D* ($\mathbf{2_s}$ and $\mathbf{3_s}$) dominate (Figures S10 and S11). Between 10 and 120 K the temperature dependence of $1/T_1$ is similar for $\mathbf{2_s}$ and $\mathbf{3_s}$, but rates for $\mathbf{3_s}$ are consistently faster than for $\mathbf{2_s}$ (Figure S13). The relaxation rates for tetraradical **1** are faster than for $\mathbf{3_s}$ or for $\mathbf{2_s}$ (conformations with small *D*), by more than an order of magnitude throughout the temperature range studied. Between 20 and 100 K the temperature dependence of $1/T_1$ for $\mathbf{2_s}$ and $\mathbf{3_s}$ is characteristic of the two-phonon Raman process. The coefficient of the contribution from the Raman process (C_{Ram}) for $\mathbf{3_s}$ is larger than that of $\mathbf{2_s}$. For mono-nitroxyls, C_{Ram} decreases as molecular increases.[S10] The larger C_{Ram} for $\mathbf{3_s}$ than for $\mathbf{2_s}$, despite its higher molecular weight, is attributed to modulation of electron-electron interaction. The larger C_{Ram} for **1** than for the conformation $\mathbf{2_s}$ and $\mathbf{3_s}$ with smaller *D* shows the importance of modulation of electron spin-spin interaction in the Raman process.

Below 20 K, $1/T_1$ for **1**, $\mathbf{2_s}$, and $\mathbf{3_s}$ is less strongly temperature dependent than at higher temperatures, which is characteristic of the direct process due to electron-electron interaction. The contribution from the direct process is greater for $\mathbf{3_s}$ than for $\mathbf{2_s}$. The molecular concentrations were about 0.3 mM, so the differences in contribution from the direct process are unlikely to be due to intermolecular interaction. The larger contribution of the direct process for $\mathbf{3_s}$ than for $\mathbf{2_s}$ is attributed to the higher spin local concentration in the octaradical than in the tetraradical.

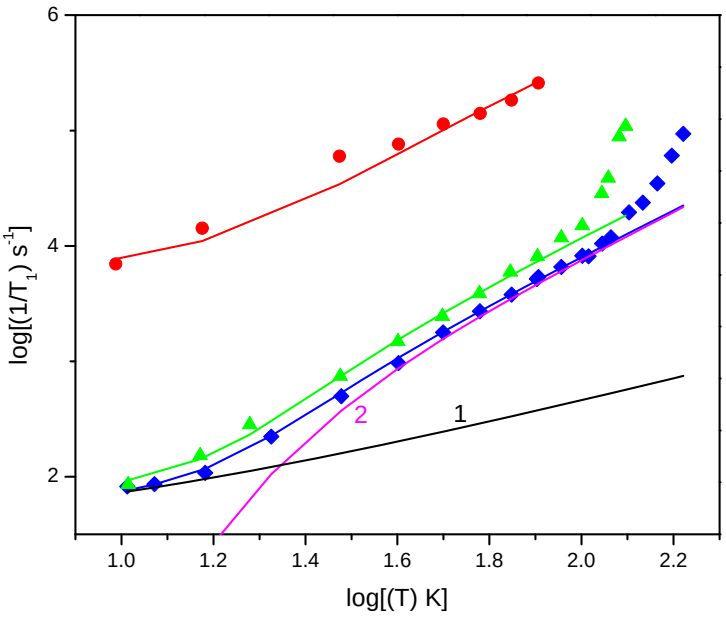


Figure S13. Temperature dependence of $1/T_1$ for **1** (●) and conformations of **2** (◆) and **3** (▲) with small *D* ($\mathbf{2_s}$ and $\mathbf{3_s}$) in 2-MeTHF/MeOH (2:1). The solid lines are the sum of the direct process (1) and the Raman process (2) for **2**.

Table S2. Parameters used to model temperature dependence of $1/T_1$.

Radical	C_{dir} [a]	C_{Ram} [b]
1 (tetraradical)	4.6×10^2 [c]	268×10^4
$\mathbf{2_s}$ (tetraradical)	4.3	5.6×10^4
$\mathbf{3_s}$ (octaradical)	5.2	8.3×10^4

[a] Direct process with constant offset parameter ($\alpha = 7$). [b] Raman process with constant Debye temperature 100 K. [c] There is substantial uncertainty in this value because of the large contribution from the Raman process even at the lowest temperature for which relaxation rates were studied.

Above about 110 K, there is strong temperature dependence of relaxation rate as the glass softens. The processes that contribute above this temperature are proposed to be tumbling

dependent. As the glass softens reorientation of the molecules modulates anisotropic interactions, which are dominated by the electron-electron interaction. The slope of the plot of $1/T_1$ vs log T is twice as large for octaradical **3** (conformation $\mathbf{3_s}$) as for tetraradical **2** (conformation $\mathbf{2_s}$), which suggests that the contribution from modulation of electron-electron interaction due to reorientation of molecules dominates. Above 80 K, the relaxation rates for **1** are too fast to measure.

5. SQUID magnetometry.

5-Tesla AC/DC SQUID magnetometer, with continuous temperature control and operating in the DC-mode, was used.

Solid octaradical **3** (8.26 mg) was loaded to the 3-piece gelatin capsule. Following the measurements, the capsule was partially emptied (1.47 mg was retained), and then identical sequences of measurements was carried out for the point-by-point correction for diamagnetism. Additional correction was based upon Pascal constants: $\chi_{dia} = -1.078\times10^{-3}$ emu mol^{-1}, as well as a small correction for residual ferromagnetic impurities. Solid tetraradical **2** (12.64 mg) was measured using similar procedure but without point-by-point correction; correction for diamagnetism was implemented by extrapolation of the χ vs. $1/T$ plots in the 180–290 K temperature range ($R^2 = 0.9998 - 1.0000$).

All solution samples were contained in home-made 5-mm O.D. EPR quality quartz tubes, modified to possess a thin bottom, which is 6 cm from the end of the tube (referred to as "SQUID tubes").[S12,S13] Tetraradical **2** (1.15 mg, or for the second sample 0.88 mg) was loaded into the SQUID tube, and then placed under vacuum. THF and/or 2-MeTHF were vacuum transferred, to obtain 8.8 mM (or for second sample 6.7 mM) concentration of tetraradical, and

after the tube was flame sealed under vacuum, the samples were carefully inserted to the magnetometer, as described elsewhere.[S12] Correction for diamagnetism was implemented by extrapolation of the χ vs. $1/T$ plots in the 60–130 K ($R^2 = 0.9998$) range.

Numerical curve fitting for magnetic data was carried out with the SigmaPlot for Windows software package. The reliability of a fit is measured by the parameter dependence, which is defined as follows: *dependence = 1 – ((variance of the parameter, other parameters constant)/(variance of the parameter, other parameters changing))*. Values close to 1 indicate overparametrized fit.

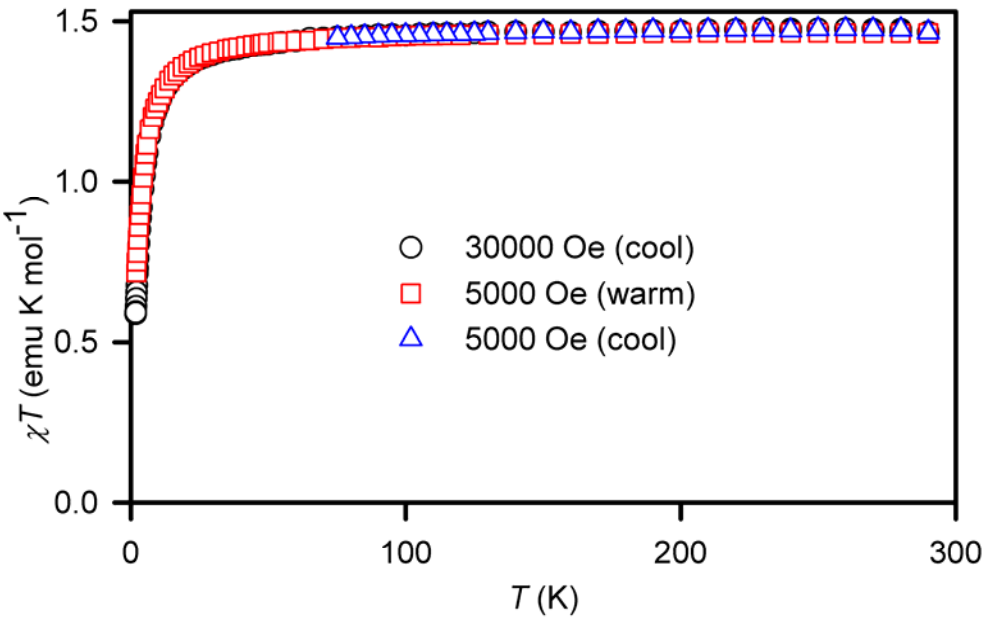


Figure S14. SQUID magnetometry of solid nitroxide tetraradical **2** (sample label: AO433col1&2, SQUID label: AO507s1).

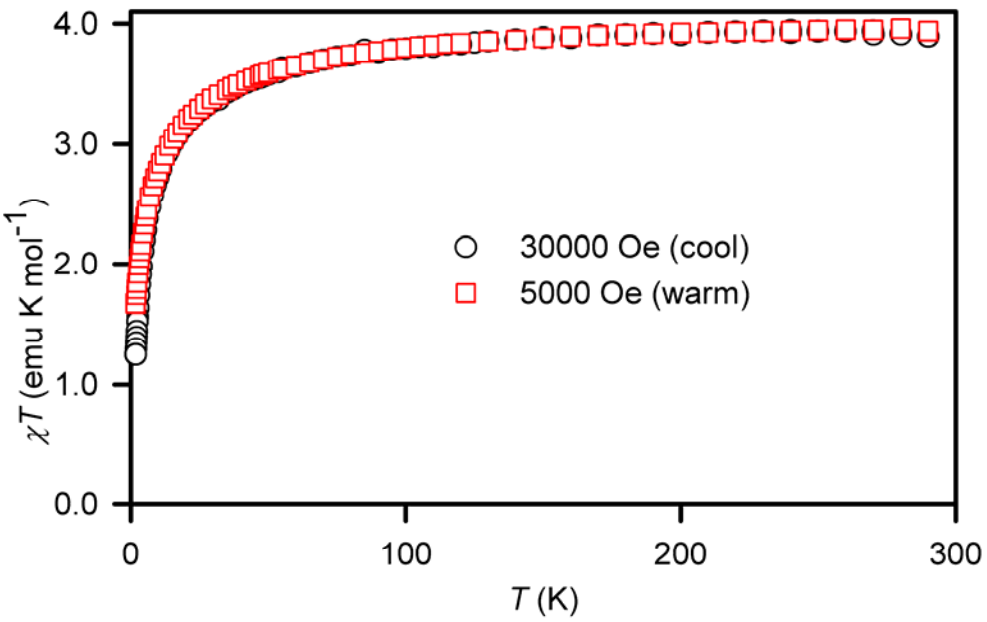


Figure S15. SQUID magnetometry of solid nitroxide octararadical **3** (sample label: AO4-37col, SQUID label: AO534s2).

6. DFT computations.

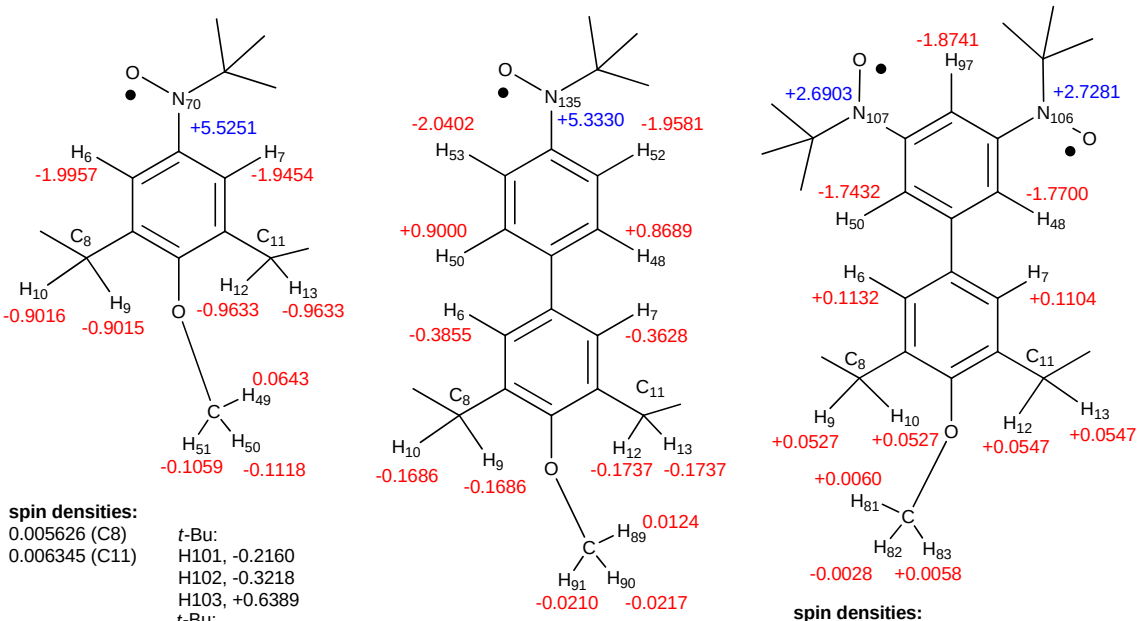
All computations were run on an 8-cpu workstation under Linux operating system. Gaussian 03 and Gaussian 09 program packages were used for geometry optimizations and frequency calculations.[S14,S15] ORCA program package and Gabedit graphical user interface were employed for calculations of EPR parameters.[S16,S17]

Geometries for high-spin states of tetraradicals **1a** and **2a**, and octaradical **3a** were fully optimized within D_2 point group of symmetry at the UB3LYP/6-31G(d) and UB3LYP/6-31G(d,p) levels of theory; **2a** was also optimized at the UB3LYP/6-31G(d) level, using IEF-PCM-UA0 solvent model for THF (Table S3 and Table S4). For all structures, dipole moments were calculated to be 0.00 D, as expected for a D_2 point group. Vibrational analyses were carried out for optimized geometries of **1a**, **2a**, and **3a** at the UB3LYP/6-31G(d) level, **1a**

optimized at the UB3LYP/6-31G(d,p) level, and **2a** optimized at the UB3LYP/6-31G(d) level using IEF-PCM-UA0 solvent model for THF; in each case, the D_2-symmetric optimized geometry was confirmed to correspond to a minimum. However, as no systematic exploration of potential energy surface was carried out, it is not known whether the optimized geometries correspond to local or global minima. All optimized geometries in the gas phase had RMS forces in Cartesian coordinates less than 6×10^{-6} a.u.; structure of **2a** optimized in IEF-PCM-UA0 solvent model for THF (Gaussian 03) had RMS forces in Cartesian coordinates less than 1.9×10^{-5} a.u. The results are summarized in Tables S3 and S4.

Spin densities, ^{1}H isotropic and ^{14}N isotropic/dipolar hyperfine coupling constants, and zero-field splitting tensors (D) for high-spin states of **1a** – **3a** were calculated at the UB3LYP/EPR-II level of theory, using ORCA. DFT grid sizes, specified by "Grid5" and "NoFinalGrid" were larger than ORCA default; e.g., for **3a**, total number of grid points (after weights and screening) was 1540877. Also, convergence criteria specified by "TightSCF", which are tighter than ORCA default, were employed.

For ORCA single-point calculations, the D_2-symmetric geometries optimized at the following levels of theory, using Gaussian 03 or Gaussian 04, were employed: gas phase, UB3LYP/6-31G(d,p) for **1a**, UA0 THF solvent model (Gaussian 03), UB3LYP/6-31G(d) for **2a**, and gas phase, UB3LYP/6-31G(d,p) for **3a**. The following zero-field splitting parameters (cm^{-1}) were obtained: **1a** ($S = 2$), $D = -0.00331$, $E = -0.00004$; **2a** ($S = 2$), $D = -0.00506$, $E = -0.00037$; **3a** ($S = 4$), $D = -0.00210$, $E = -0.00015$. Values of isotropic ^{1}H hyperfine coupling constants ($A(^{1}H)$) are summarized in Fig. S16.



spin densities:
0.005626 (C8)
0.006345 (C11)

t-Bu:
H101, -0.2160
H102, -0.3218
H103, +0.6389
t-Bu:
H105 1.0360
H106, -0.3860
H107, -0.4009
t-Bu:
H109, 0.2082
H110, -0.4056
H111, +0.0724

spin densities:
0.001036 (C8)
0.001320 (C11)

t-Bu:
H140, -0.3285
H141, -0.3182
H142, +0.9883
t-Bu:
H143, -0.2446
H144, +0.6784
H145, -0.3206
t-Bu:
H146, -0.4039
H147, +0.2359
H148, +0.0825

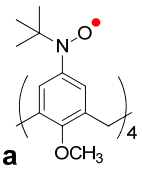
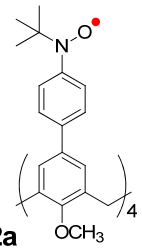
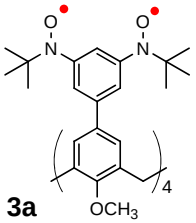
spin densities:
-0.000730 (C8)
-0.000712 (C11)

t-Bu:
H145, +0.3674
H146, -0.1146
H147, +0.1057
t-Bu:
H177, +0.1229
H178, -0.2153
H179, +0.0038
t-Bu:
H189, -0.1845
H190, +0.5390
H191, -0.1446

t-Bu:
H141, -0.2229
H142, -0.1632
H143, +0.6387
t-Bu:
H173, -0.2408
H174, +0.0818
H175, -0.0554
t-Bu:
H201, -0.0814
H202, -0.1145
H203, +0.1473

Figure S16. Isotropic hyperfine couplings (MHz) and spin densities, computed at the UB3LYP/EPR-II level of theory using ORCA for high-spin states of **1a**, **2a**, and **3a**. ^{1}H hyperfine couplings (red) and ^{14}N hyperfine couplings (blue) are taken directly from ORCA outputs, i.e., not scaled for values of *S*. ^{1}H hyperfine couplings for *tert*-butyl groups are listed below the structures. Spin densities from ORCA sum to the number of unpaired electrons, i.e., four for **1a** and **2a**, and eight for **3a**.

Table S3. UB3LYP energies (E°, hartree), zero point vibrational energies (ZPVE, hartree), spin operator expectation values ($\langle S^2 \rangle$), lowest vibrational frequencies (cm^{-1}), and RMS gradient norms (a.u.) at the optimized geometries within the D_2-point group of symmetry.

Structure	 **1a**	 **2a**	 **3a**
Basis set	6-31G(d)	6-31G(d)	6-31G(d)
E° (gas phase)	-2688.14288501	-3612.37501081	-4760.98909877
ZPVE	1.054602	1.379941	1.863268
$\langle S^2 \rangle$	6.0496	6.0538	20.1142
RMS gradient norm[a] ($\times 10^{-6}$)	0.552	0.599	1.70
Lowest vibrational frequencies	21.7 (B3), 24.5 (A), 27.5 (B2)	12.9 (B1), 13.2 (B2), 15.8 (A)	11.6 (A), 14.3 (B3), 14.8 (B2)
Basis set	6-31G(d,p)	6-31G(d,p)	6-31G(d,p)
E° (gas phase)	-2688.23369702	-3612.49077302	-4761.14951755
ZPVE	1.050601	-	-
$\langle S^2 \rangle$	6.0499	6.0539	20.1152
RMS gradient norm[a] ($\times 10^{-6}$)	5.58	2.51	0.160
Lowest vibrational frequencies	20.8 (B3), 23.6 (A), 27.1 (B2)	-	-
Basis set		6-31G(d)	
E° (THF)		-3612.39443871	
ZPVE		1.378568	
$\langle S^2 \rangle$		6.0544	
RMS gradient norm[a] ($\times 10^{-6}$)		19	
Lowest vibrational frequencies		14.8 (B1), 15.3 (B2), 20.5 (A)	

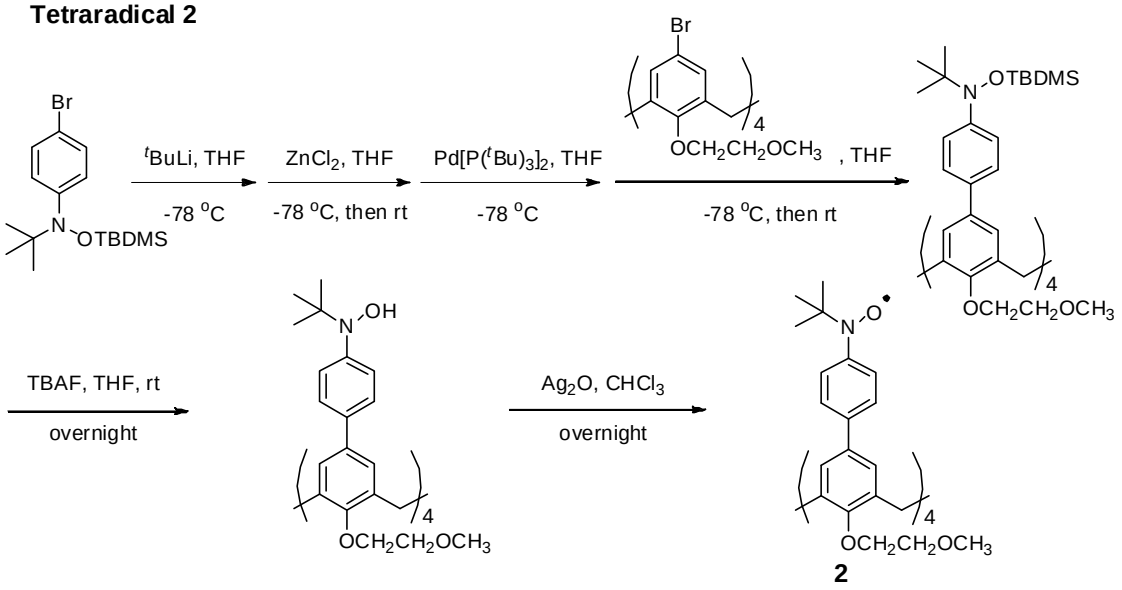
[a] Cartesian coordinates.

Table S4. Selected torsional angles (°) and intramolecular distances (Å) for calix[4]arene nitroxides.

		Biphenyl	Cofacial				Adjacent	
	ONCC	CCCC	C···C	C···C	N···N	O···O	N···N	O···O
Tetraradical **1**[S13] (X-ray structure)	15.1, -163.8 -55.7, 121.6 -41.4, 132.8 36.8, -138.1	-	-	5.48 5.49	5.78 5.70	6.92 6.05	9.34 9.34 9.45 9.50	10.12 10.34 10.67 10.74
Tetraradical **1a** UB3LYP/6-31G(d) gas phase	-10.0, 167.2	-	-	4.87	4.58	4.66	9.13 9.18	9.64 10.59
Tetraradical **1a** UB3LYP/6-31G(d,p) gas phase	-9.4, 167.9	-	-	4.86	4.58	4.68	9.13 9.18	9.65 10.60
Tetraradical **2a** UB3LYP/6-31G(d) gas phase	7.6, -171.5	-32.8, -35.1	4.55	4.98	4.40	4.29	17.44 17.57	18.15 18.64
Tetraradical **2a** UB3LYP/6-31G(d,p) gas phase	7.1, -172.1	-32.6, -35.0	4.53	4.97	4.38	4.27	17.43 17.56	18.14 18.63
Tetraradical **2a** UB3LYP/6-31G(d) THF	11.0, -167.8	-32.0, -34.5	4.66	5.01	4.58	4.67	17.45 17.60	18.14 18.72
Octaradical **3a** UB3LYP/6-31G(d) gas phase	-16.5, 162.8 26.0, -151.5	-28.4, -30.6	6.13	5.46	6.00 6.11	6.76 6.86	14.37 14.62 15.05 15.71 15.79 16.63	12.88 16.06 16.22 16.43 17.00 18.29
Octaradical **3a** UB3LYP/6-31G(d,p) gas phase	25.1, -152.5, -15.6, 163.7	-28.8, -30.9	6.12	5.45	5.97 6.10	6.70 6.87	14.38 14.62 15.04 15.70 15.78 16.63	12.87 16.05 16.22 16.43 17.01 18.28

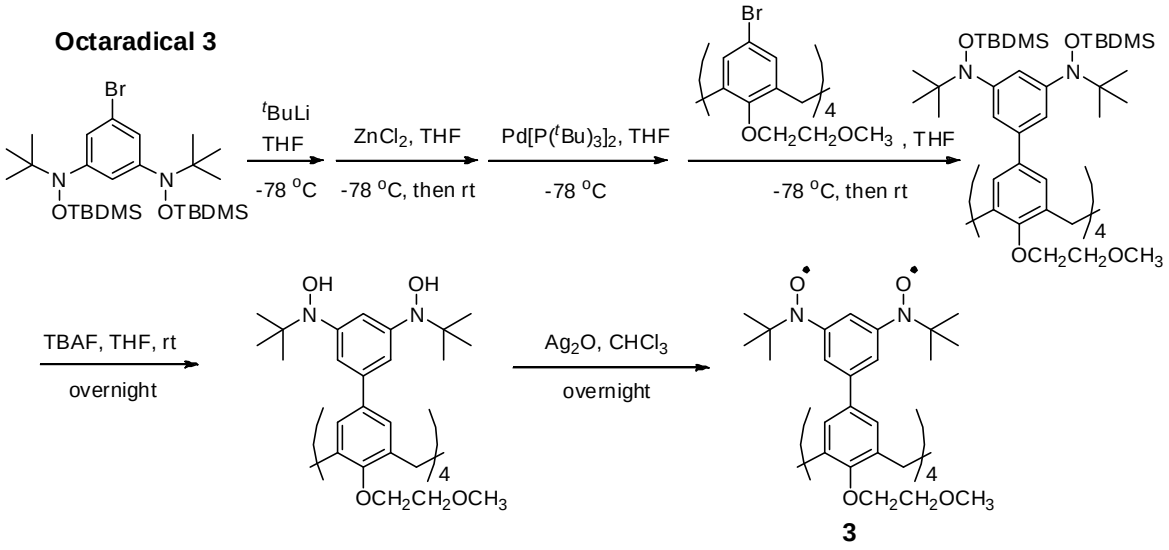
7. Synthesis of nitroxide tetraradical 2 and octaradical 3.

Tetraradical 2

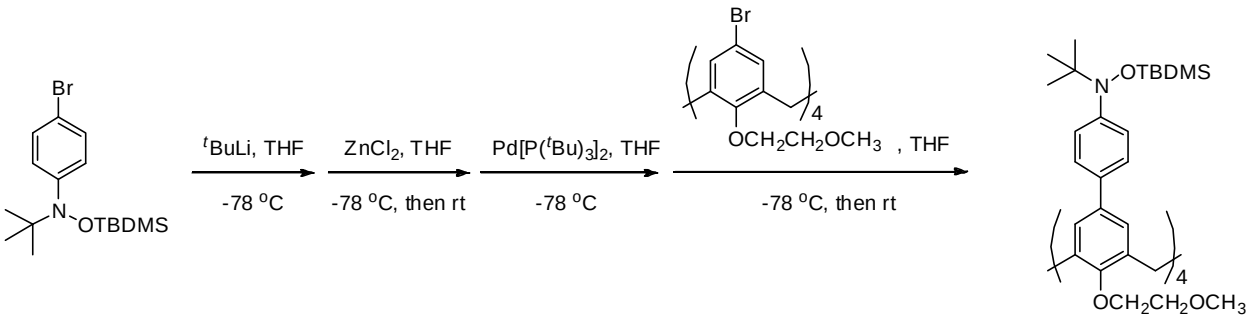


2

Octaradical 3



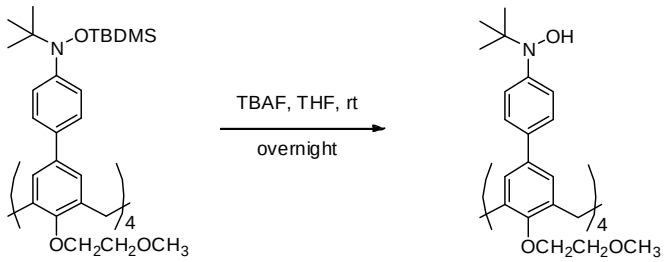
3



Run	N-OTBDMS (mg, mmol)	^{t}BuLi (mL, mmol)	1 M $ZnCl_2$ (mL, mmol)	Pd[P(^{t}Bu$_3$)$_2$] (mg, mmol)	Tetrabromocalixarene (mg, mmol)	Yield (mg, %)
AO-3-77	130, 0.362	0.48, 0.76	4.4, 4.34	25, 0.048	59, 0.060	26, 24
AO-3-87	170, 0.474	0.63, 1.00	5.7, 5.69	32, 0.063	77, 0.079	52, 37
AO-4-27	253, 0.698	0.92, 1.46	8.4, 8.37	48, 0.093	113, 0.116	60, 29

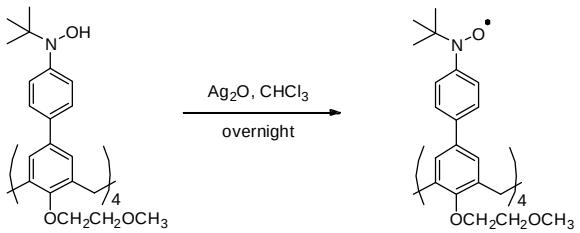
Negishi coupling: TBDMS-protected tetrahydroxylamine 6 (AO-3-87). The procedure for Negishi coupling of TBDMS-protected hydroxylamine **5** with protected iodo-nucleoside was followed, with minor modifications.[S18] TBDMS-protected hydroxylamine **5** (170.0 mg, 0.474 mmol), tetrabromocalix[4]arene **4**[S13] (76.9 mg, 0.0791 mmol) were introduced separately in the screw capped Schlenk vessels equipped with magnetic stirring bars and dried for overnight. Freshly distilled THF (2 mL) was added to both of the starting materials under N_2 flow. *t*-BuLi in pentane (1.59 M, 0.63 mL, 0.996 mmol) was added dropwise to a solution of TBDMS-protected hydroxylamine **5** at –78 °C under N_2 flow. The resulting yellow solution was stirred at –78 °C for 2 h. A solution of $ZnCl_2$ (1.00 M, 5.7 mL, 5.69 mmol) was added dropwise under N_2 flow at –78 °C. The resulting solution was warmed to the ambient temperature to obtain a clear organo-zinc solution for 10 min and then was cooled to at –78 °C. Pd[P(*t*-Bu)$_3$]$_2$ (32.3 mg, 0.0632 mmol) was weighed and transferred into a Schlenk vessel inside the glove box. The Pd catalyst solution was prepared by adding freshly distilled THF (1 mL) into the Schlenk vessel under N_2 flow. This catalyst solution was added to the organo-zinc solution under N_2 flow at –78 °C. The solution of the tetrabromocalix[4]arene **4** was added dropwise to the reaction mixture

under N_2 flow at –78 °C. The reaction mixture was stirred at room temperature for 72 h. The resulting solution was filtered through a Celite pad and concentrated in vacuo to give a crude mixture. The crude was purified by column chromatography (silica gel, ethyl acetate/pentane, 5:95) to give the desired Negishi coupling product **6** (52.0 mg, 37%) as a white solid. M.p. 218-220 °C (under air). ^{1}H NMR (600 MHz, chloroform-*d*, AO-3-87-col1): δ = 7.518 (d, J = 8.4 Hz, 8H), 7.394 (s, 8H), 7.265 (br, 8H), 4.012 (s, 8H), 3.701 (t, J = 6.6 Hz, 8H), 2.875 (t, J = 6.6 Hz, 8H), 2.800 (s, 12H), 1.098 (s, 36H), 0.901 (s, 36H), –0.124 (br, 24H). ^{13}C NMR (150 MHz, chloroform-*d*, AO-3-87-col1): δ = 155.4, 149.9, 136.9, 134.8, 134.3, 127.3, 125.4, 125.2, 70.4, 67.9, 60.9, 58.6, 38.4, 26.1, 26.1, 17.9, –4.8. IR (ZnSe, cm^{-1}, AO-3-87-col1): 2956, 2926, 2850, 1466, 1387, 1359, 1246, 1120, 1125, 1082, 1036, 944, 860, 834, 780. LRFAB–MS (ONPOE matrix, AO-3-77-col1): *m/z* ion type (%RA for *m/z* = 600-2500): 1766 $[M+H]^+$ (100%). HRFAB–MS (ONPOE matrix, AO-3-77-col1): *m/z* ion type (%RA for *m/z* = 1762-1770): 1767.0952 $[M+2H]^+$ (77%, 0.1 ppm for $^{12}C_{104}{}^{1}H_{158}{}^{14}N_4{}^{16}O_{12}{}^{28}Si_4$), 1766.0908 $[M+H]^+$ (100%, –1.9 ppm for $^{12}C_{104}{}^{1}H_{157}{}^{14}N_4{}^{16}O_{12}{}^{28}Si_4$), 1765.0852 $[M]^+$ (69%, –3.1 ppm for $^{12}C_{104}{}^{1}H_{156}{}^{14}N_4{}^{16}O_{12}{}^{28}Si_4$).



Run	SM (mg, mmol)	TBAF (mL, mmol)	Yield (mg, %)	TM label
AO-3-85	2.5, 0.00142	0.013, 0.0130	0.9, 49	AO-3-85-flt1
AO-3-90	25.6, 0.0145	0.14, 0.133	18.0, 95	AO-3-90-flt
AO-4-07	52.0, 0.0294	0.28, 0.271	35.7, 93	AO-4-07-flt
AO-4-31	60.0, 0.0340	0.31, 0.312	44, 100	AO-4-31-flt

Tetrahydroxylamine 7 (AO-4-31). TBAF (0.31 mL, 0.312 mmol) was added dropwise to a solution of TBDMS-protected tetrahydroxylamine **6** (60.0 mg, 0.0340 mmol) in freshly distilled THF (2 mL). The resultant solution was protected from light and stirred at room temperature for overnight (20 h). The crude mixture was rapidly filtered through a silica gel pad using ethyl acetate (100 mL). Concentration in vacuo and drying under high vacuum gave the tetrahydroxylamine **7** (44.4 mg, 100%) as a red solid. M.p. 225-228 °C (brown liquid). ^{1}H NMR (500 MHz, acetone-d_6, AO-3-90-flt): δ = 9.116 (d, J = 8.5 Hz, 4H), 7.462 (s, 8H), 7.204 (br d, $J \approx 8$ Hz, 8H), 6.886 (br d, $J \approx 8$ Hz, 8H), 4.001-3.909 (m, 16H), 3.661 (s, 8H), 3.576 (s, 12H), 1.207 (s, 36H). ^{1}H NMR (500 MHz, chloroform-*d*, AO-4-31-flt): δ = 9.336 (s, 4H), 7.372 (s, 8H), 7.110 (br, 8H), 6.843 (br, 8H), 3.991-3.856 (m, 16H), 3.608 (s, 8H), 3.560 (s, 12H), 1.206 (s, 36H). IR (ZnSe, cm^{-1}, AO-3-90-flt): 3232, 2961, 2924, 2872, 1466, 1454, 1389, 1362, 1233, 1200, 1172, 1124, 1081, 1057, 1029, 835, 800. LRFAB–MS (3-NBA matrix, AO-3-85-flt): *m/z* ion type (%RA for *m/z* = 500-2000): 1310 $[M+H]^+$ (100%). HRFAB–MS (3-NBA matrix, AO-3-85-flt): *m/z* ion type (%RA for *m/z* = 1306-1312): 1309.7391 $[M+H]^+$ (90%, 1.9 ppm for $^{12}C_{80}{}^{1}H_{101}{}^{14}N_4{}^{16}O_{12}$), 1308.7362 $[M]^+$ (100%, –1.9 ppm for $^{12}C_{80}{}^{1}H_{100}{}^{14}N_4{}^{16}O_{12}$).



Run	SM (mg, mmol)	Ag_2O (mg, mmol)	Yield (mg, %)	TM label
AO-3-89	1.5, 0.00115	10.6, 0.0458	N.A.	N.A.
AO-3-93	18.3, 0.0140	130.0, 0.559	7.8, 43	AO-3-95-col
AO-4-10	35.7, 0.0273	253.0, 1.090	5.6, 16	AO-4-20-colfr2-3
AO-4-33	44.4, 0.0339	315.0, 1.358	23.0, 52	AO-4-33-col

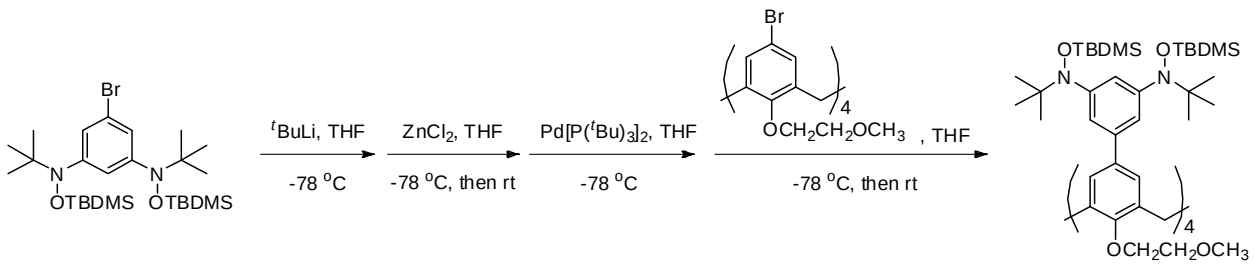
Nitroxide tetraradical 2 (AO-4-33). Freshly prepared silver oxide (315.0 mg, 1.36 mmol) was added to a solution of tetrahydroxylamine **7** (44.4 mg, 0.0339 mmol) in chloroform (2 mL).

After being stirred at room temperature in darkness for 20 h, the reaction mixture was filtered through a cotton plug. The red filtrate was evaporated to dryness to give the crude product. The crude was purified by column chromatography (silica gel, chloroform/ethyl acetate, 4:1) to give the nitroxide tetraradical **2** (23.0 mg, 52%) as a red solid. M.p. 130 °C (dec.). ^{1}H NMR (500 MHz, chloroform-*d*, AO-4-33-col1&2-500, conc. 77.1 mM): δ = 4.00–3.63 (br, br, 28H), –3.18 (br, 36H), –5.42 (br, 8H), –13.95 (br, 8H). ^{1}H NMR (500 MHz, chloroform-*d*, AO-4-20-colfr2-3, conc. 5.7 mM): δ = 3.53–3.18 (br, br, 28H), –3.67 (br, 44H). IR (ZnSe, cm^{-1}, AO-4-20-colfr2-3): 2981, 2929, 2875, 1585, 1466, 1455, 1364, 1237, 1176, 1125, 1082, 1057, 1032, 831, 756. LRFAB–MS (3-NBA matrix, AO-4-20-colfr2-3): *m/z* ion type (%RA for *m/z* = 500-1600): 1309 $[M+4H]^+$ (100%). HRFAB–MS (3-NBA matrix, AO-4-20-colfr2-3): *m/z* ion type (%RA for *m/z* = 1304-1313): 1308.7362 $[M+4H]^+$ (100%, –1.9 ppm for $^{12}C_{80}{}^{1}H_{100}{}^{14}N_4{}^{16}O_{12}$), 1307.7271 $[M+3H]^+$ (49%, –0.9 ppm for $^{12}C_{80}{}^{1}H_{99}{}^{14}N_4{}^{16}O_{12}$).

Summary of EPR spin concentration measurements for tetraradical **2** at 294–295 K.

Run	Sample	Solvent, Concentration	Double Integration	SW[a]	Spin Conc.	Avg. χT emuK/mol
AO421r1	AO-4-20-colfr2-3	Chloroform, 1.5 mM	3.84e7	400	3.79	1.46
AO421r3	4-Oxo-TEMPO	Chloroform, 1.5 mM	2.53e8	80		
AO421r1	AO-4-20-colfr2-3	Chloroform, 1.5 mM	3.84e7	400	3.62	
AO421r2	4-Oxo-TEMPO	Chloroform, 1.5 mM	1.06e7	400		
AO559r1	AO-4-33-col1&2	Chloroform, 1.5 mM	7.076e7	400	4.28	
AO560r1	3-Carboxy-PROXYL	Chloroform, 1.5 mM	1.654e7	400		

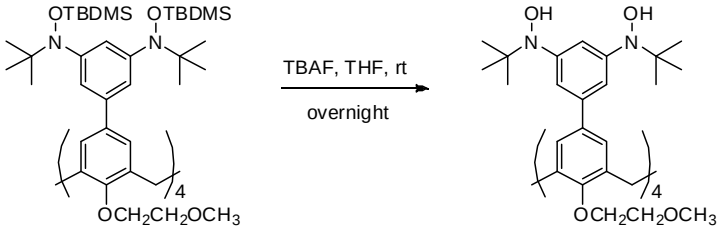
[a] SW = sweep width



Run	N-OTBDMS (mg, mmol)	^{t}BuLi (mL, mmol)	1 M $ZnCl_2$ (mL, mmol)	Pd[P(^{t}Bu$_3$)$_2$] (mg, mmol)	Tetrabromocalixarene (mg, mmol)	Yield (mg, %)
AO-3-63	146, 0.261	0.35, 0.548	3.2, 3.132	17.8, 0.0348	42.0, 0.0435	17.0, 15
AO-3-72	209, 0.374	0.50, 0.785	4.5, 4.485	25.5, 0.0498	61.0, 0.0623	32.0, 7
AO-3-88	420, 0.750	1.00, 1.576	9.0, 9.00	51.1, 0.100	122.0, 0.125	
AO-4-13	466, 0.833	1.10, 1.75	10.0, 10.0	57.0, 0.111	135.0, 0.139	8.7, 2
AO-4-17	518, 0.926	1.25, 1.94	11.1, 11.1	63.0, 0.123	150.0, 0.154	99.8, 25
AO-4-49	411, 0.734	1.04, 1.54	8.8, 8.81	50.0, 0.0979	119.0, 0.122	79.6, 25

Negishi coupling: TBDMS-protected octahydroxylamine 9 (AO-4-17). TBDMS-protected dihydroxylamine **8** (518.0 mg, 0.926 mmol), tetrabromocalix[4]arene **4**[S13] (150.0 mg, 0.154 mmol) were introduced separately in the screw capped Schlenk vessels equipped with magnetic stirring bars and dried for overnight. Freshly distilled THF (10 mL) was added to both of the starting materials under N_2 flow. *t*-BuLi in pentane (1.56 M, 1.25 mL, 1.94 mmol) was added dropwise to a solution of TBDMS-protected dihydroxylamine **8** at –78 °C under N_2 flow. The resulting yellow solution was stirred at –78 °C for 2 h. A solution of $ZnCl_2$ (1.00 M, 11.1 mL, 11.1 mmol) was added dropwise under N_2 flow at –78 °C. The resulting solution was warmed to the ambient temperature to obtain a clear organo-zinc solution for 10 min and then was cooled to at –78 °C. Pd[P(*t*-Bu)$_3$]$_2$ (63.0 mg, 0.123 mmol) was weighed and transferred into a Schlenk vessel inside the glove box. The Pd catalyst solution was prepared by adding freshly distilled THF (2 mL) into the Schlenk vessel under N_2 flow. The resulting catalyst solution was added to the organo-zinc solution under N_2 flow at –78 °C. The solution of the tetrabromocalix[4]arene **4** was added dropwise to the reaction mixture under N_2 flow at –78 °C. The reaction mixture was stirred at room temperature for 48 h. The resulting solution was filtered through a Celite pad and

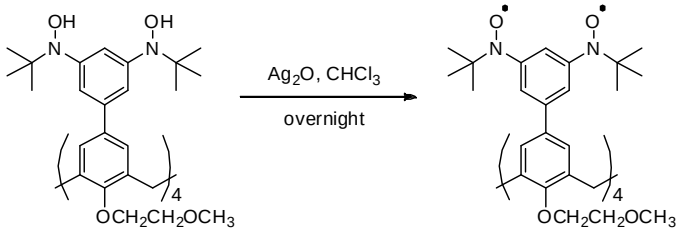
concentrated in vacuo to give a crude mixture. The crude was purified by column chromatography (silica gel, ethyl acetate/pentane, 1:200) to give the desired Negishi coupling product **9** (99.8 mg, 25%) as a white solid. M.p. 265 °C (dec.). ^{1}H NMR (400 MHz, chloroform-*d*, AO-3-88-hv): δ = 7.315 (br, 20H), 4.017 (s, 8H), 3.572 (br, 8H), 2.911 (br, 20H), 1.120 (s, 72H), 0.950 (s, 72H), –0.050 (br, 48H). ^{13}C NMR (100 MHz, chloroform-*d*, AO-3-88-hv): δ = 155.9, 150.6, 138.5, 135.3, 134.1, 127.7, 120.0, 70.6, 68.9, 61.0, 58.9, 38.5, 26.3, 26.1, 17.9, –4.5. IR (ZnSe, cm^{-1}, AO-3-88-hv): 2956, 2927, 2855, 1591, 1577, 1472, 1438, 1387, 1358, 1246, 1197, 1129, 1090, 1026, 952, 892, 854, 833, 778, 734. LRFAB–MS (ONPOE matrix, AO-3-66-colfr1): *m/z* ion type (%RA for *m/z* = 800-3500): 2572 $[M+2H]^+$ (100%). HRFAB–MS (ONPOE matrix, AO-3-66-colfr1): *m/z* ion type (%RA for *m/z* = 2568-2576): 2571.7024 $[M+2H]^+$ (100%, 4.9 ppm for $^{12}C_{144}{}^{1}H_{250}{}^{14}N_8{}^{16}O_{16}{}^{28}Si_8$), 2570.6996 $[M+H]^+$ (83%, 2.9 ppm for $^{12}C_{144}{}^{1}H_{249}{}^{14}N_8{}^{16}O_{16}{}^{28}Si_8$), 2569.7001 $[M]^+$ (41%, –0.3 ppm for $^{12}C_{144}{}^{1}H_{248}{}^{14}N_8{}^{16}O_{16}{}^{28}Si_8$).



Run	SM (mg, mmol)	TBAF (mL, mmol)	Yield (mg, %)	TM label
AO-3-91	10.5, 0.00408	0.076, 0.0751	6.0, 89	AO-3-91-flt
AO-4-08	28.0, 0.0109	0.20, 0.200	15.7, 87	AO-4-08-flt
AO-4-25	8.7, 0.00338	0.063, 0.0622	5.3, 95	AO-4-25-flt
AO-4-29	29.2, 0.0114	0.21, 0.209	18.2, 97	AO-4-29-flt
AO-4-58	21.9, 0.00851	0.16, 0.157	10.9, 77	AO-4-58-flt

Octahydroxylamine 10 (AO-4-29). TBAF (0.21 mL, 0.209 mmol) was added dropwise to a solution of TBDMS-protected octahydroxylamine **9** (29.2 mg, 0.0114 mmol) in freshly distilled

THF (1 mL). The resultant solution was protected from light and stirred at room temperature for overnight (20 h). The crude mixture was rapidly filtered through a silica gel pad using chloroform (100 mL). Concentration in vacuo and drying under high vacuum gave the octahydroxylamine **10** (18.2 mg, 97%) as a yellow solid. M.p. 160 °C (dec.). ^{1}H NMR (400 MHz, chloroform-*d*, AO-3-91-flt): δ = 9.028 (br, 8H), 7.419 (s, 12H), 7.162 (br, 8H), 4.035 (s, 16H), 3.641 (s, 8H), 3.624 (s, 12H), 1.221 (s, 36H). IR (ZnSe, cm^{-1}, AO-3-88-hv): 3172, 2965, 2925, 2872, 2850, 1594, 1442, 1390, 1361, 1257, 1199, 1161, 1125, 1090, 1048, 1025, 951, 902, 868, 801, 731. LRFAB–MS (3-NBA matrix, AO-3-91-flt): *m/z* ion type (%RA for *m/z* = 600-2500): 1658 $[M+H]^+$ (100%). HRFAB–MS (3-NBA matrix, AO-3-91-flt): *m/z* ion type (%RA for *m/z* = 1655-1662): 1658.0079 $[M+H]^+$ (100%, 4.4 ppm for $^{12}C_{96}{}^{1}H_{137}{}^{14}N_{8}{}^{16}O_{16}$), 1657.0039 $[M]^+$ (71%, 2.2 ppm for $^{12}C_{96}{}^{1}H_{136}{}^{14}N_{8}{}^{16}O_{16}$).



Run	SM (mg, mmol)	Ag_2O (mg, mmol)	Yield (mg, %)	TM label
AO-3-94	6.0, 0.00362	34.0, 0.145	5.0, 84	AO-3-94-wsh
AO-4-11	15.7, 0.00947	176.0, 0.757	no reaction	n.a.
AO-4-28	5.3, 0.00320	30.0, 0.128	2.9, 55	AO-4-28-col
AO-4-30	18.2, 0.0110	102.0, 0.439	10.8, 60	AO-4-32-col
AO-4-37	40.7, 0.0245	227.8, 0.982	21.7, 54	AO-4-37-col

Nitroxide octaradical 3 (AO-4-30). Freshly prepared silver oxide (102.0 mg, 0.439 mmol) was added to a solution of octahydroxylamine **10** (18.2 mg, 0.0110 mmol) in chloroform (2 mL). After being stirred at room temperature in darkness for 20 h, the reaction mixture was filtered through a cotton plug. The yellow filtrate was evaporated to dryness to obtain the crude product. The crude product was purified by column chromatography (silica gel, ethyl acetate/pentane,

1:1) to give nitroxide octaradical **3** (10.8 mg, 60%) as an orange solid. M.p. 150 °C (dec.). ^{1}H NMR (500 MHz, chloroform-*d*, AO-4-37-col, conc. 60.2 mM): δ = 22.91 (br, 8H), 12.44 (br, 8H), 4.74–4.17 (br, br, 28H), –2.80 (br, 72H). ^{1}H NMR (500 MHz, chloroform-*d*, AO-4-32-col, conc. 43.6 mM): δ = 11.93 (br, 8H), 4.19–3.60 (br, br, 28H), –3.38 (br, 72H). IR (ZnSe, cm^{-1}, AO-4-32-col): 2981, 2874, 2817, 1581, 1476, 1444, 1267, 1249, 1192, 1125, 1047, 859, 743, 706. LRFAB–MS (3-NBA matrix, AO-4-32-col): *m/z* ion type (%RA for *m/z* = 700-1900): 1658 $[M+8H]^+$ (100%). HRFAB–MS (3-NBA matrix, AO-4-32-col): *m/z* ion type (%RA for *m/z* = 1653-1662): 1657.0081 $[M+8H]^+$ (100%, –0.4 ppm for $^{12}C_{96}{}^{1}H_{136}{}^{14}N_{8}{}^{16}O_{16}$), 1656.0079 $[M+7H]^+$ (67%, –5.0 ppm for $^{12}C_{96}{}^{1}H_{135}{}^{14}N_{8}{}^{16}O_{16}$).

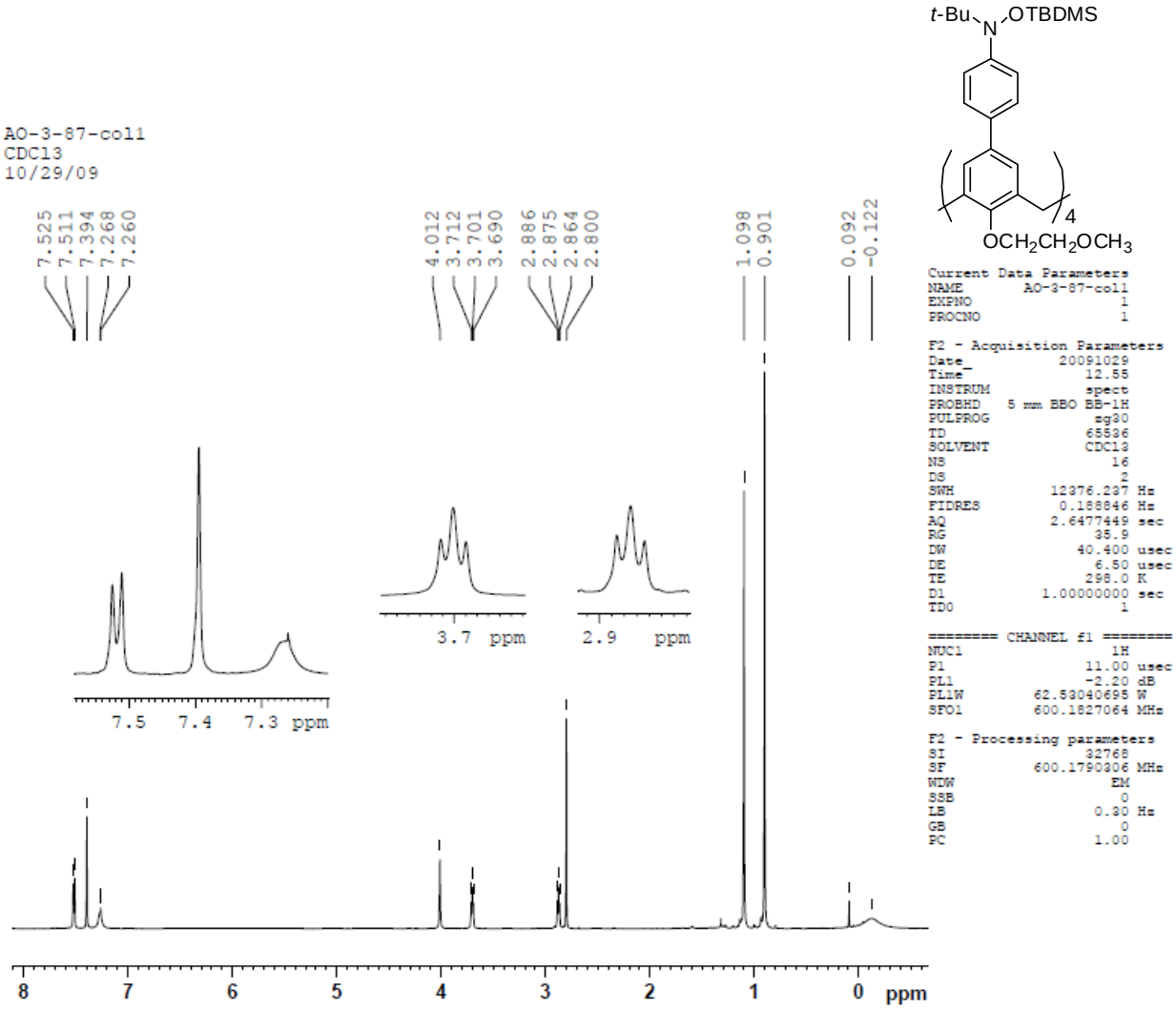
Summary of EPR spin concentration measurement for octaradical **3**.

Run	Sample	Solvent, Concentration	Double Integration	SW[a]	Spin Conc.	Spin Conc. × 0.75/2.0 χT [emuK/mol]
AO558r1	AO-4-37-col	Chloroform, 1.5 mM	1.703e8	400	10.3	3.86
AO560r1	3-Carboxy-PROXYL	Chloroform, 1.5 mM	1.654e7	400		

[a] SW = sweep width

8. ^{1}H NMR, ^{13}C NMR, and IR spectra for synthesis of 2 and 3.

^{1}H NMR in chloroform-*d*

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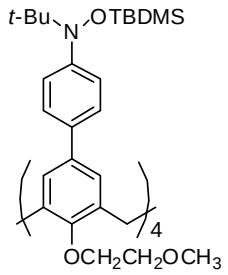
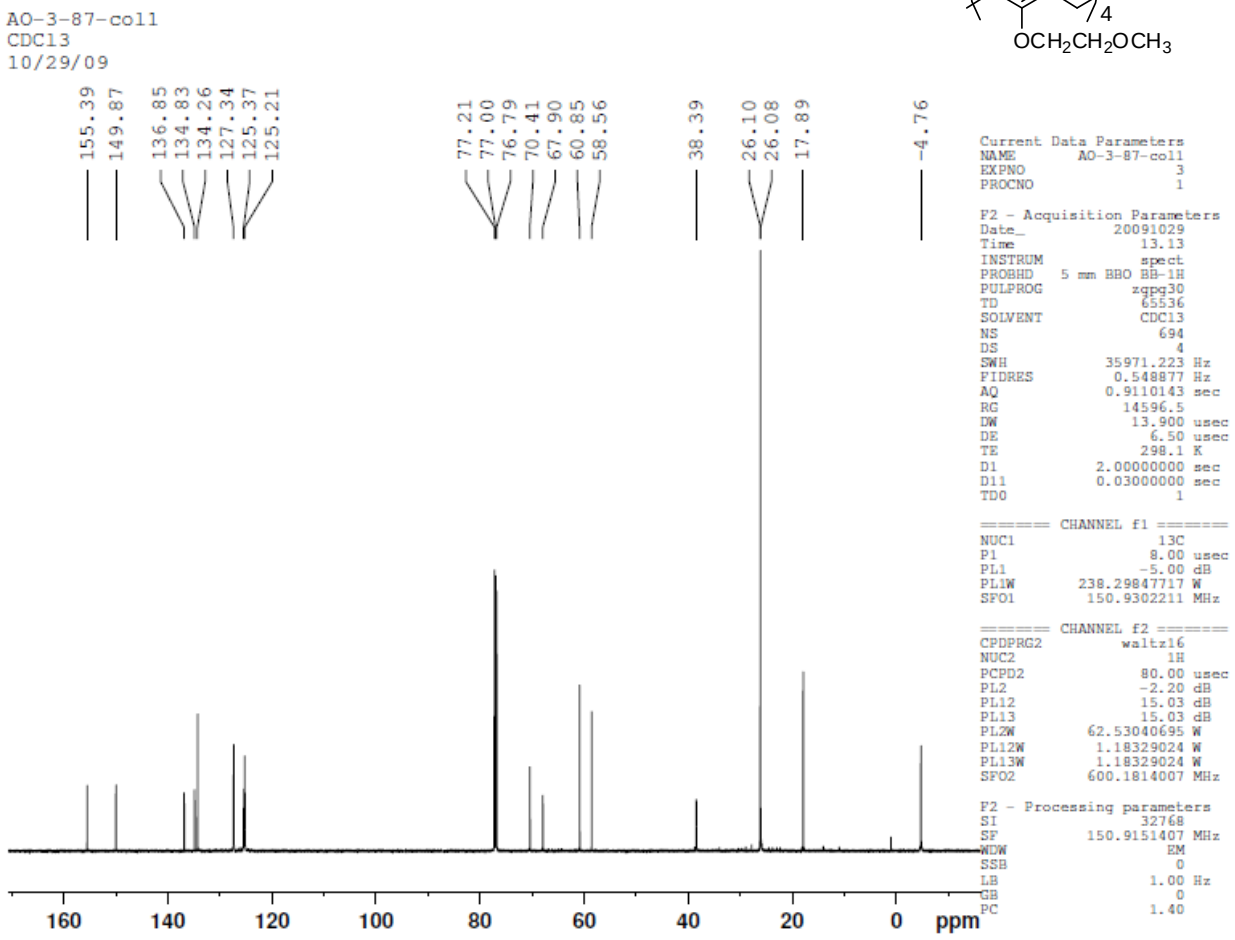
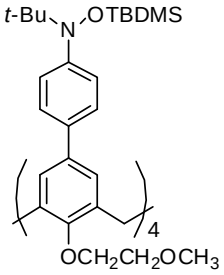
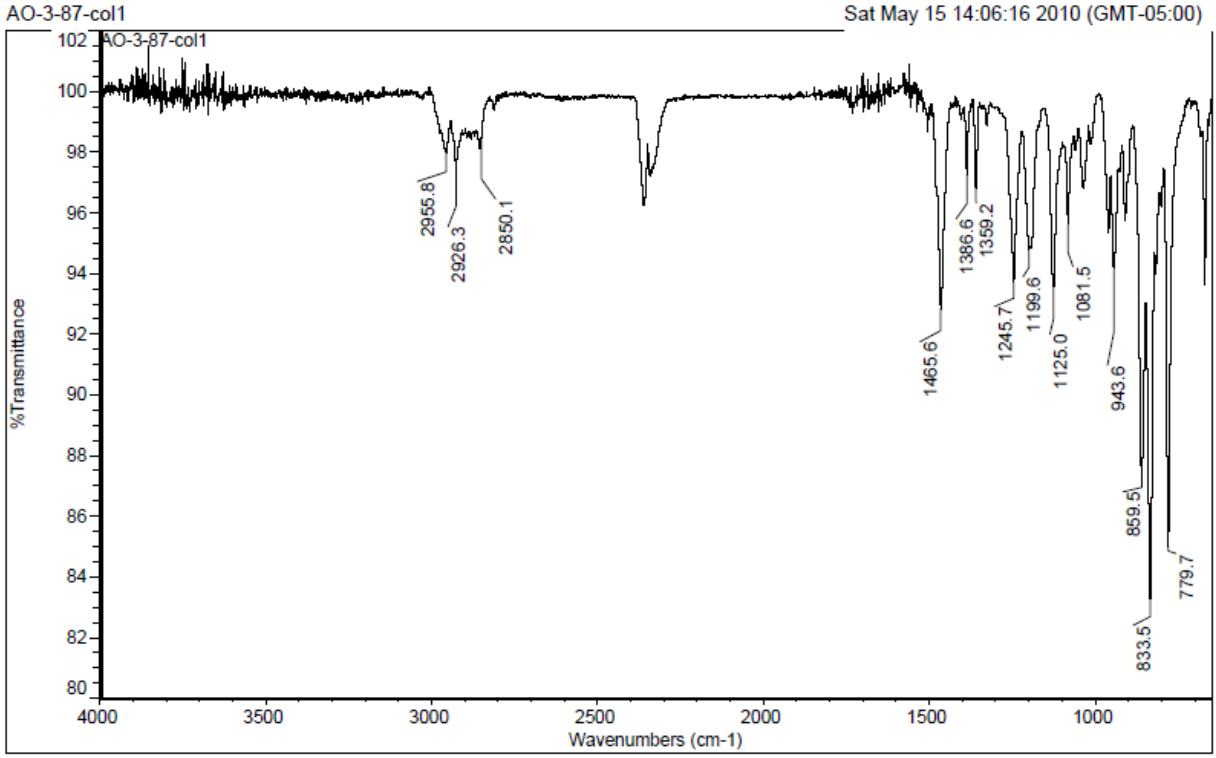
^{13}C NMR in chloroform-*d*





IR





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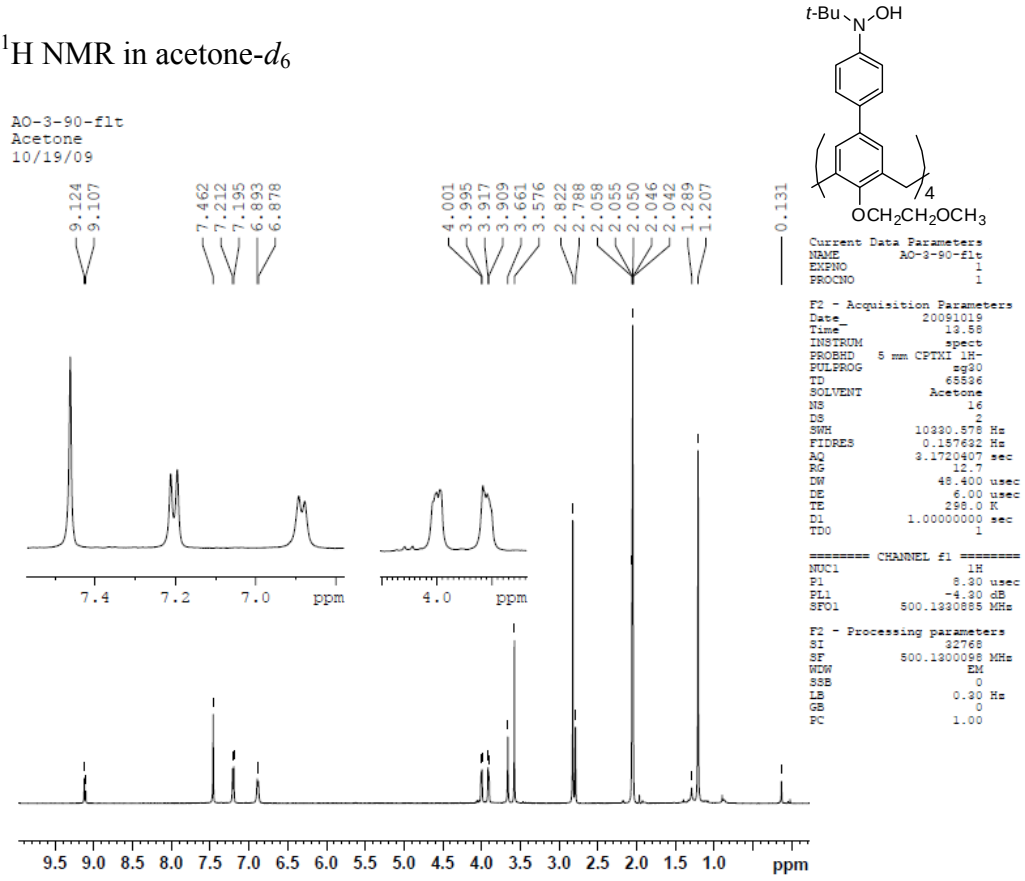
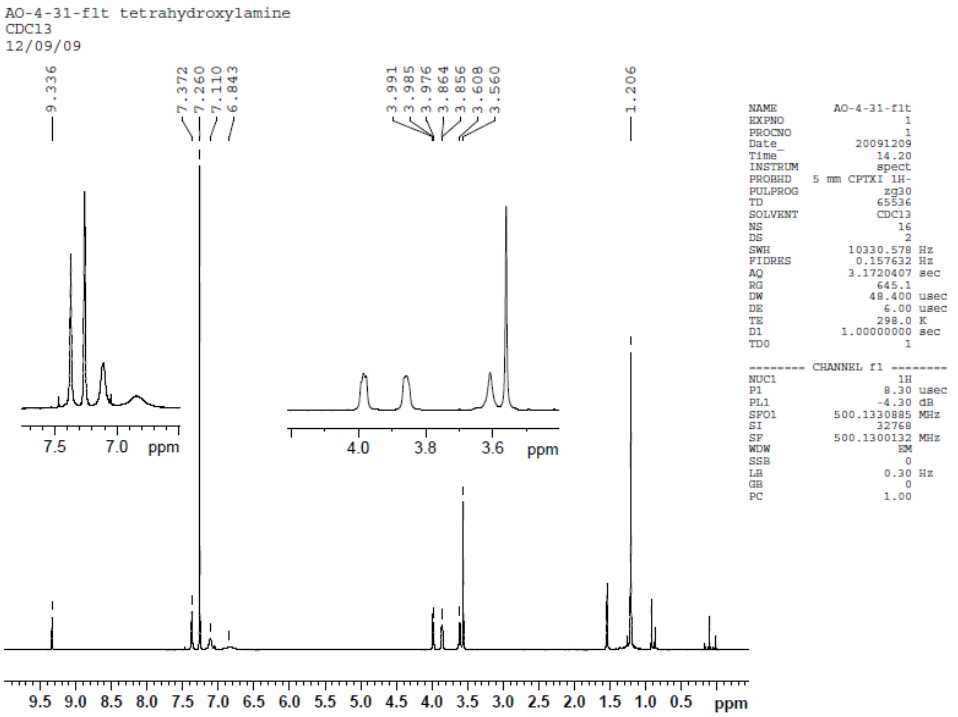
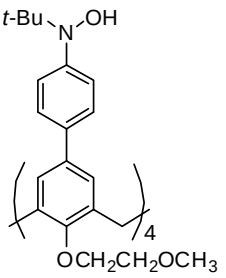
^{1}H NMR in acetone-d_6

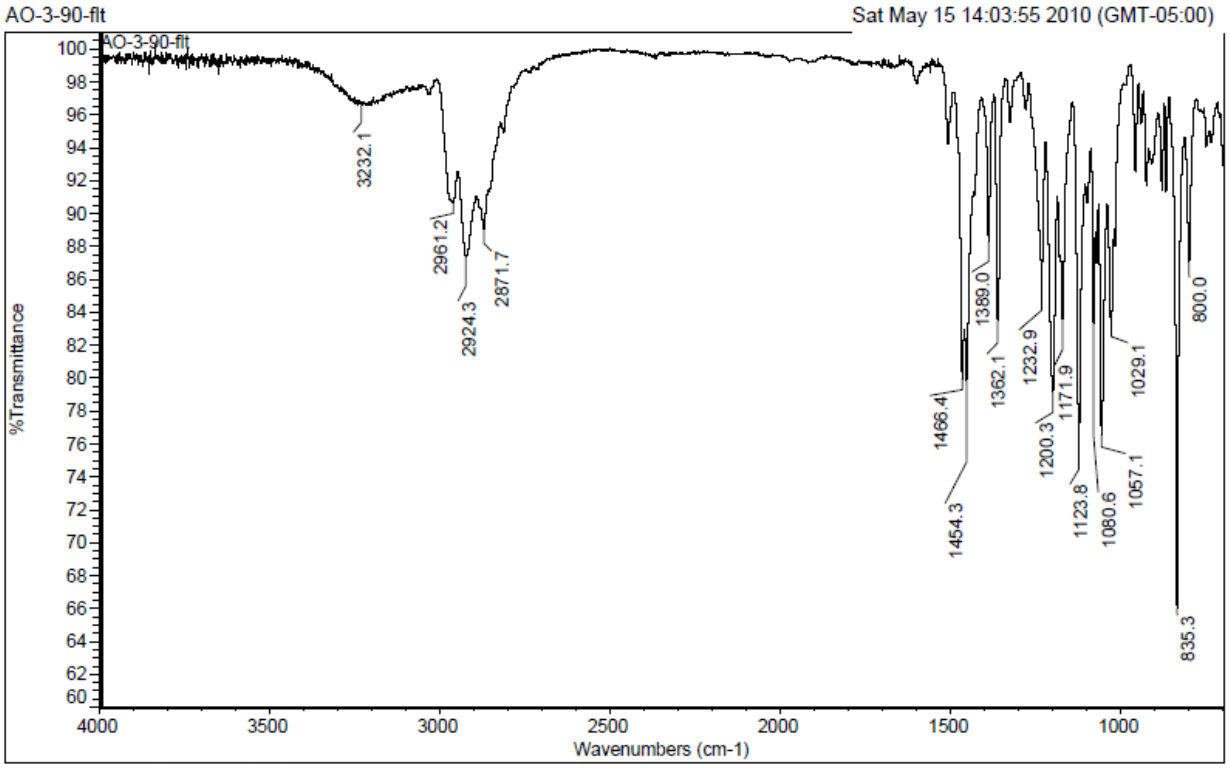


^{1}H NMR in chloroform-d



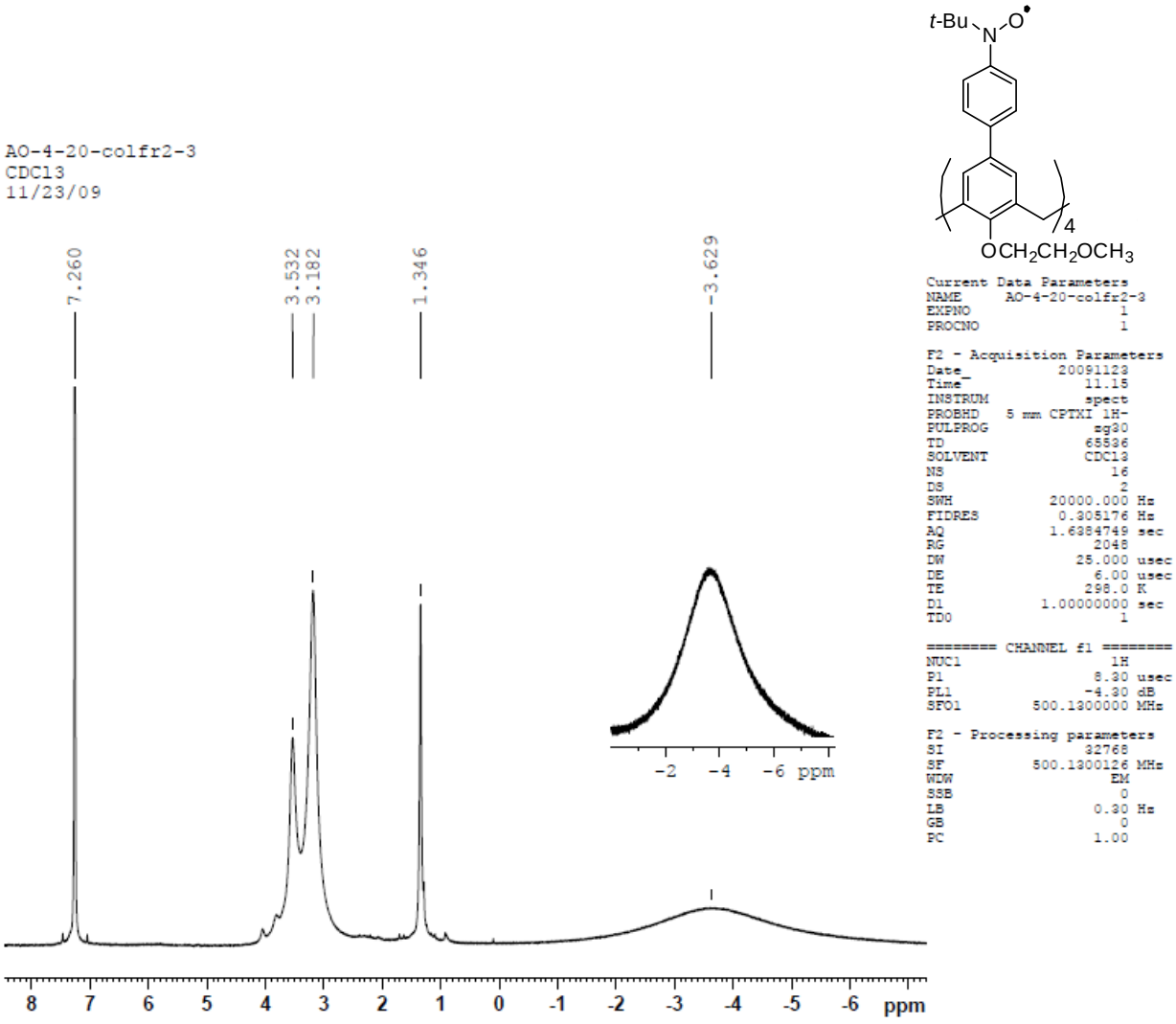
IR



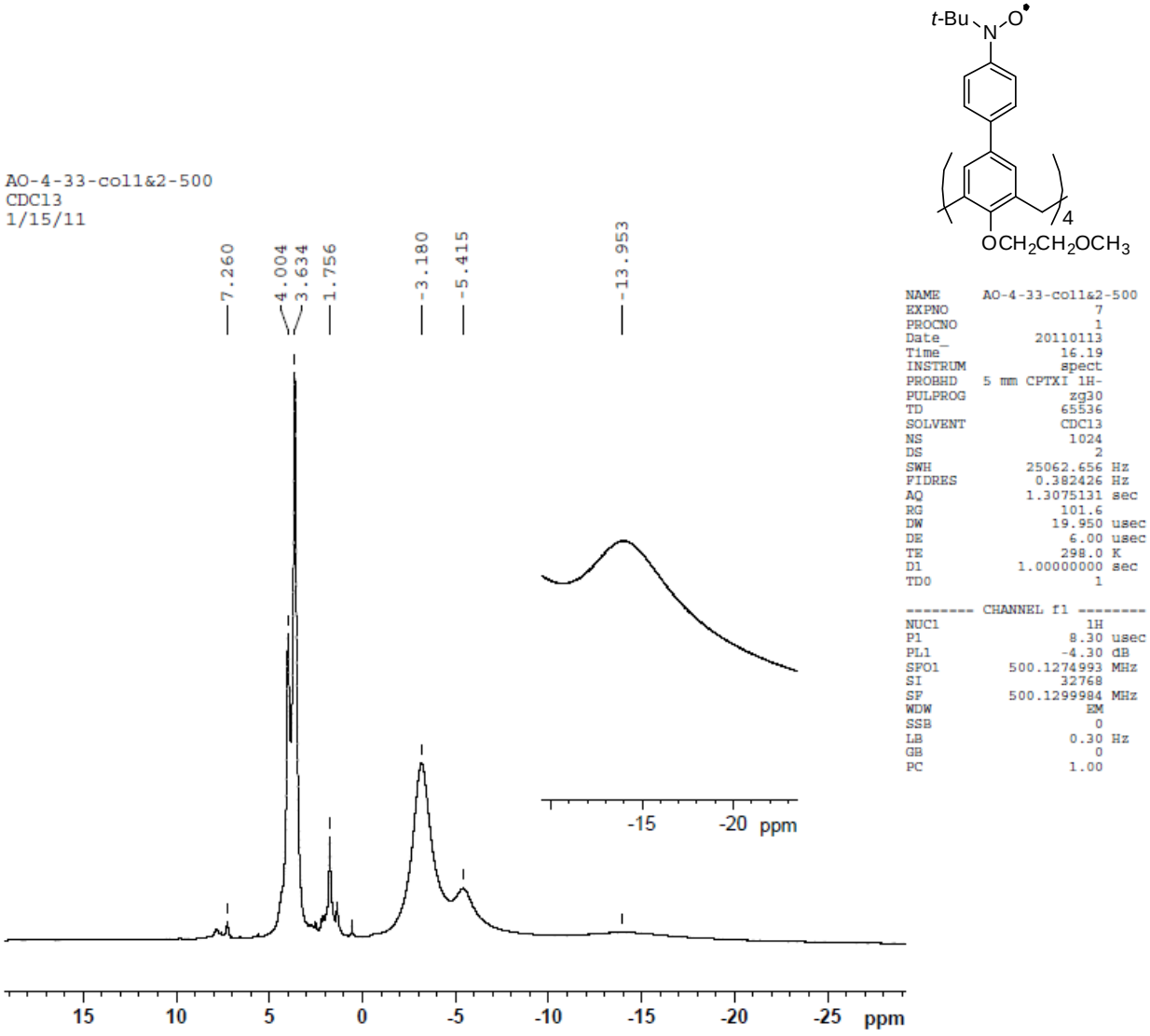


Number of sample scans: 128
Number of background scans: 128
Resolution: 2.000
Sample gain: 1.0
Optical velocity: 0.6329
Aperture: 100.00

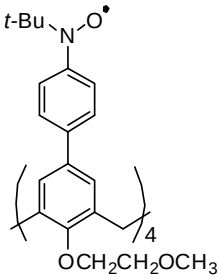
^{1}H NMR in chloroform-*d*

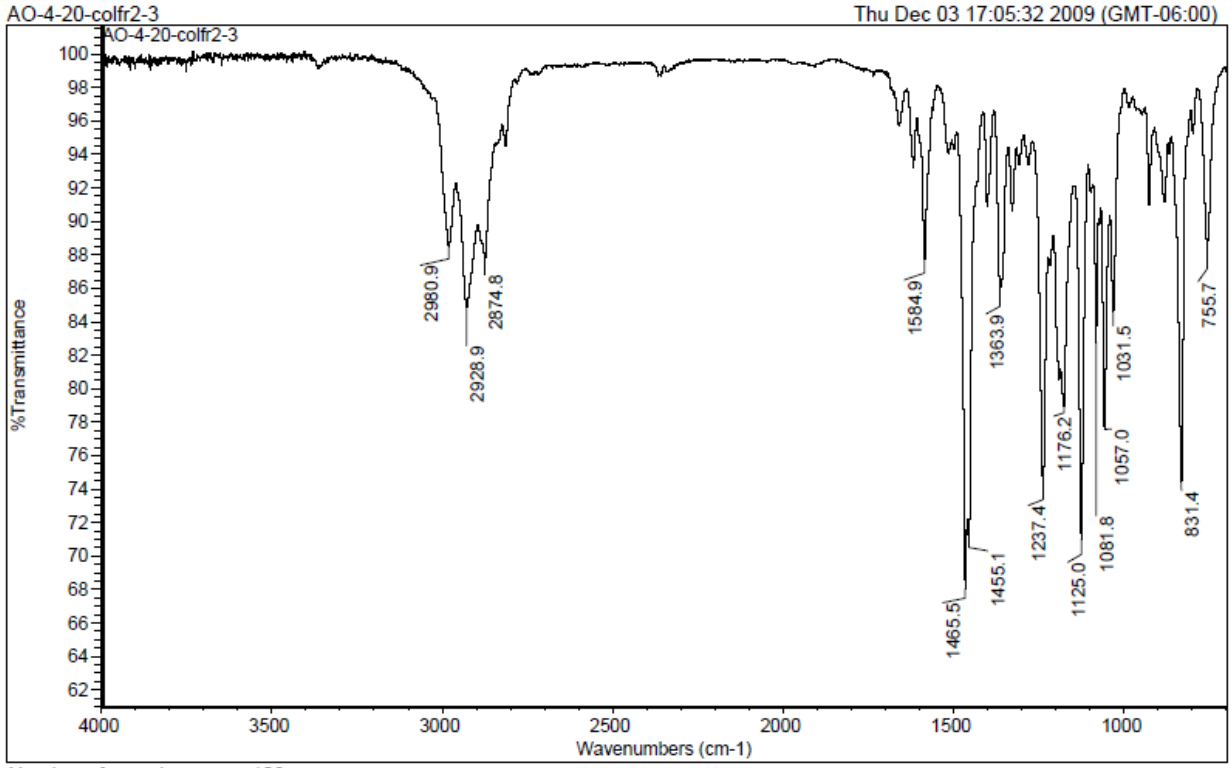


^{1}H NMR in chloroform-*d*



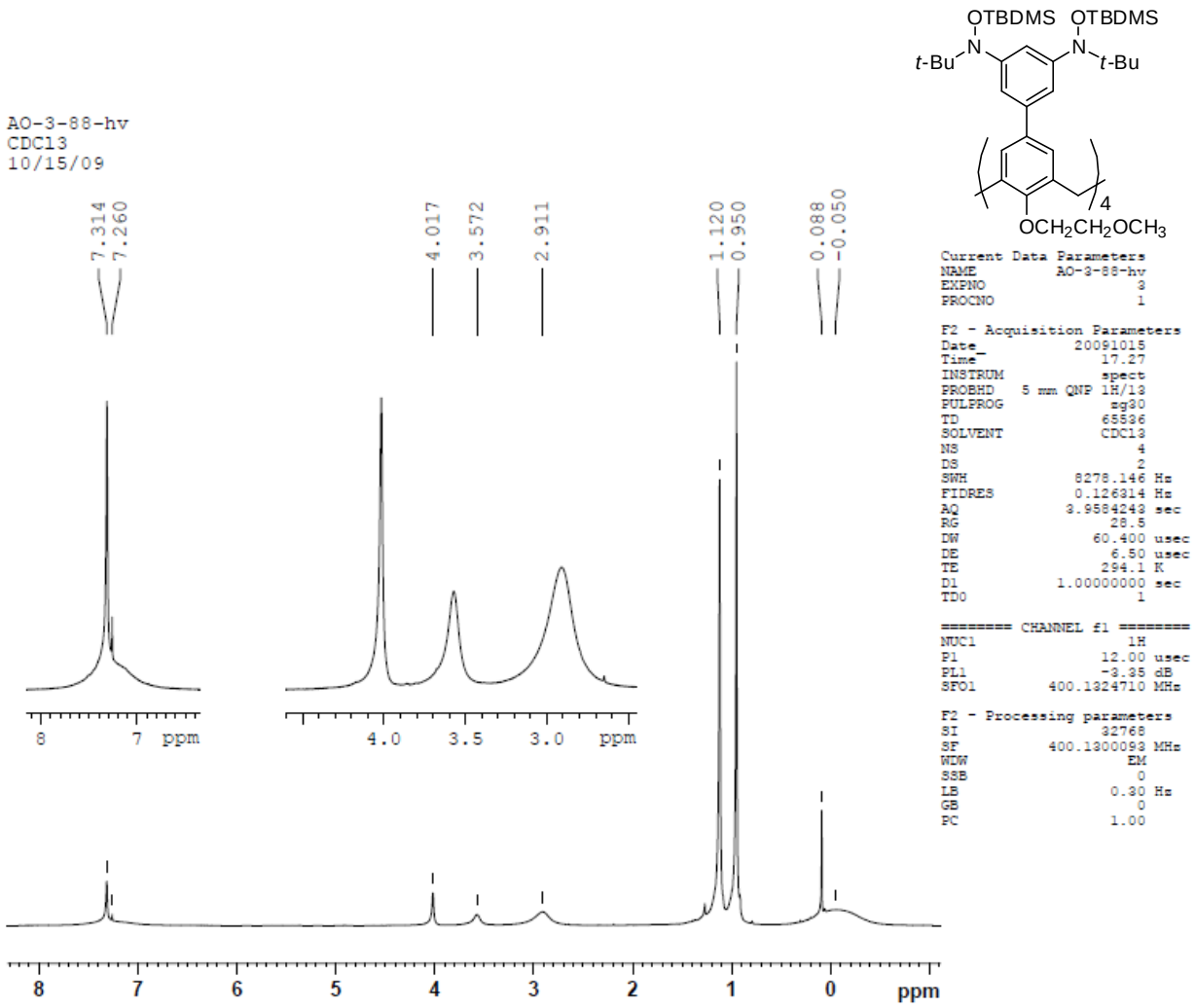
IR



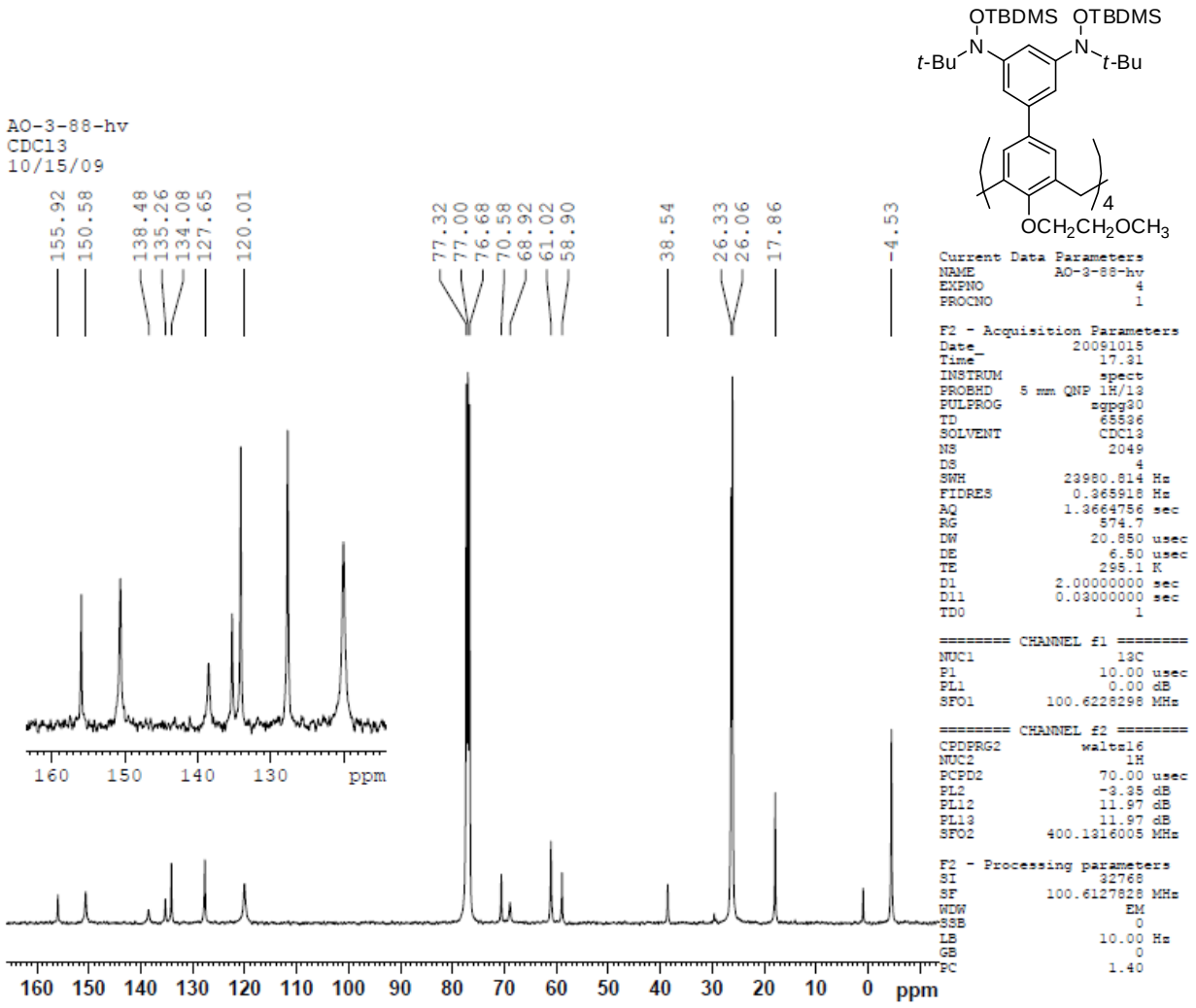


Number of sample scans: 128
Number of background scans: 128
Resolution: 2.000
Sample gain: 1.0
Optical velocity: 0.6329
Aperture: 100.00

^{1}H NMR in chloroform-*d*



^{13}C NMR in chloroform-*d*



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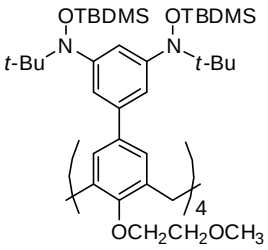
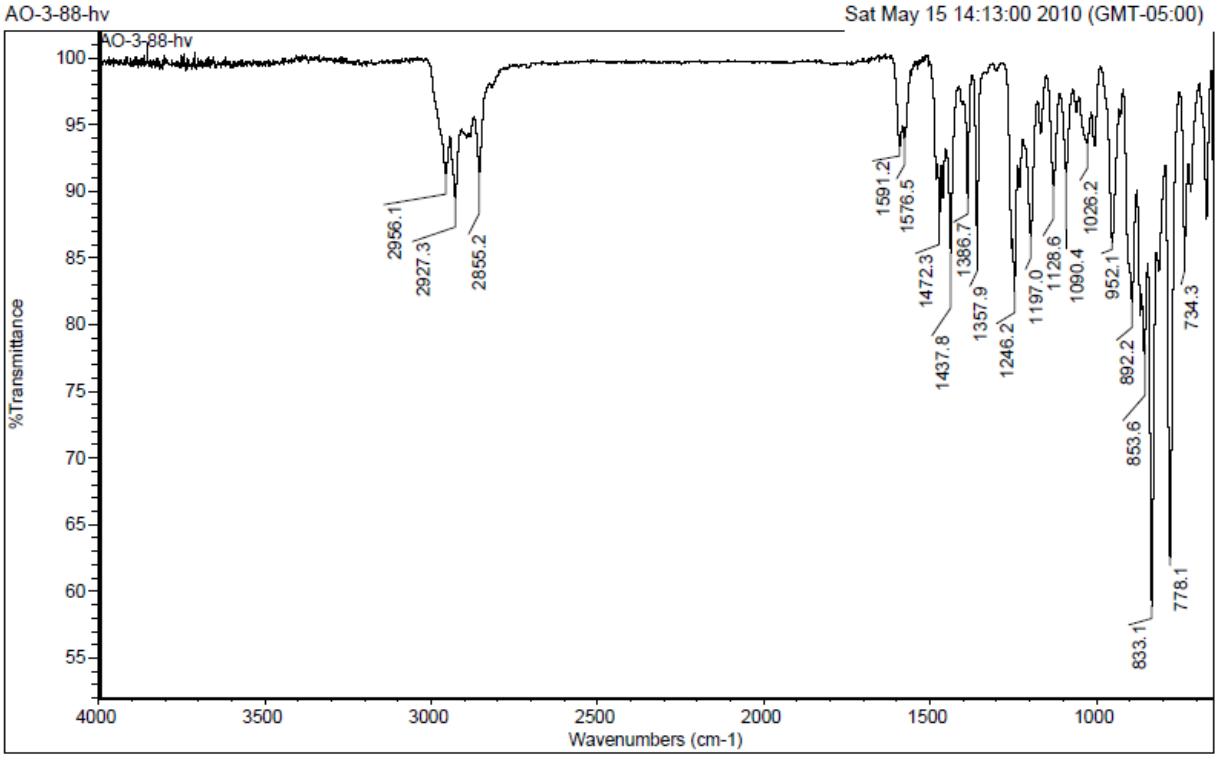
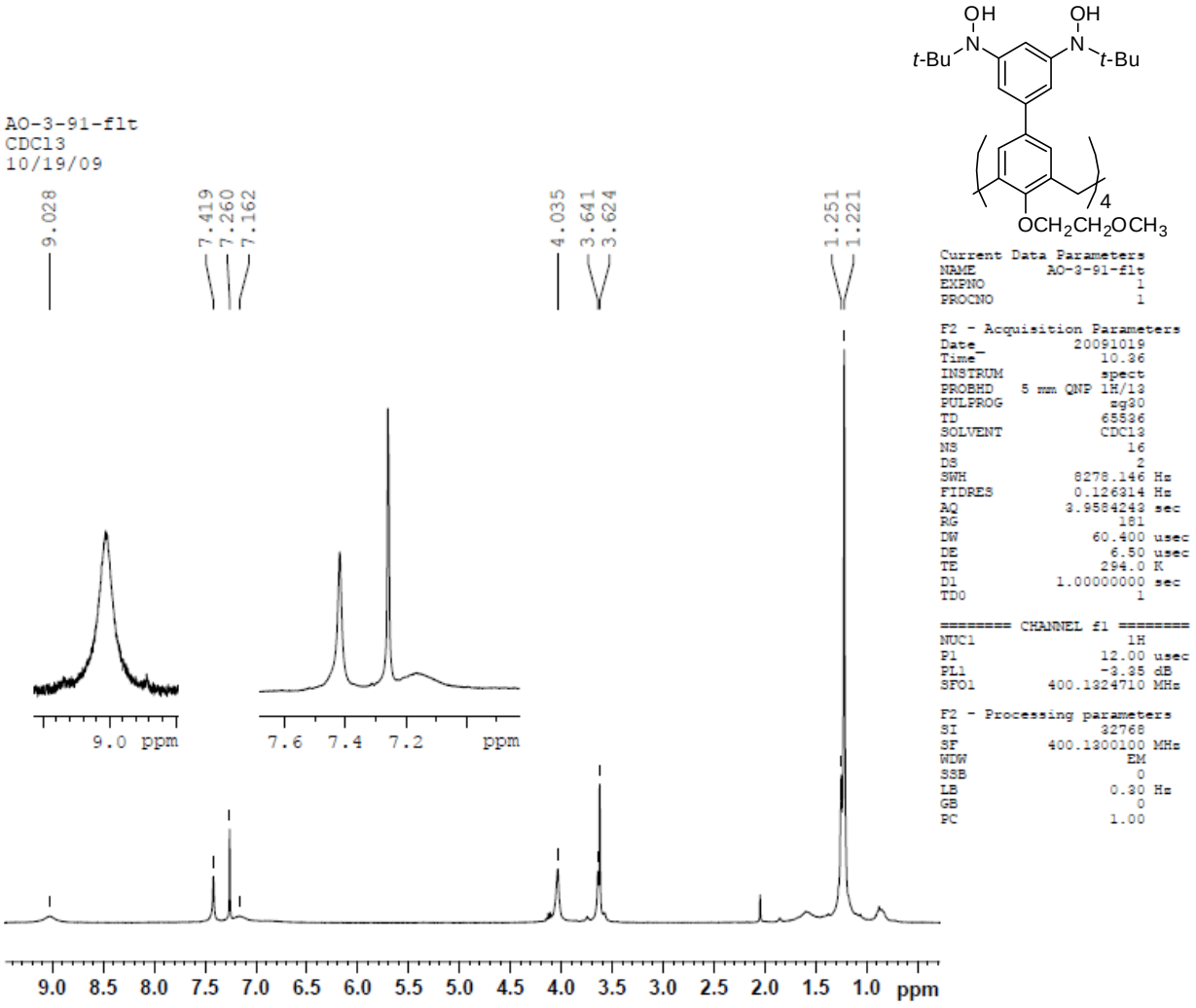




Number of sample scans: 128
Number of background scans: 128
Resolution: 2.000
Sample gain: 1.0
Optical velocity: 0.6329
Aperture: 100.00

^{1}H NMR in chloroform-*d*



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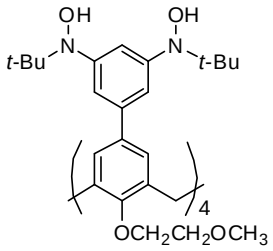
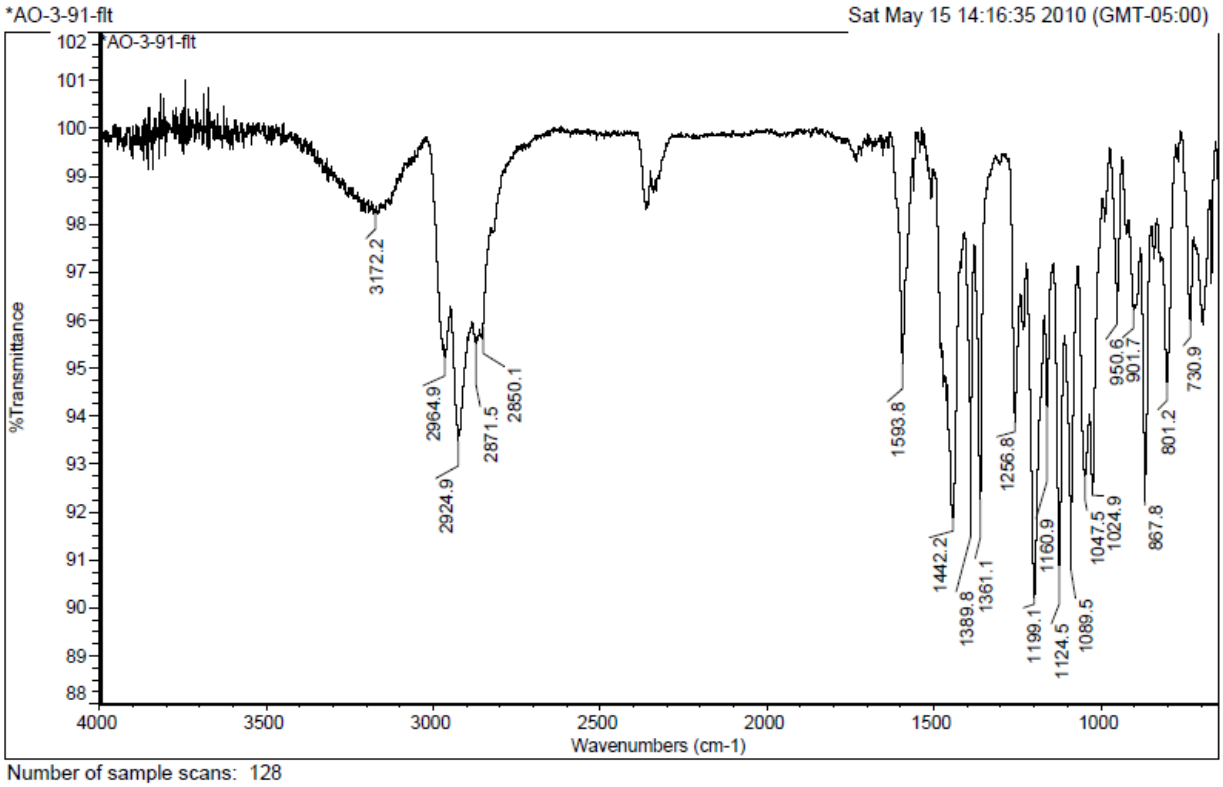
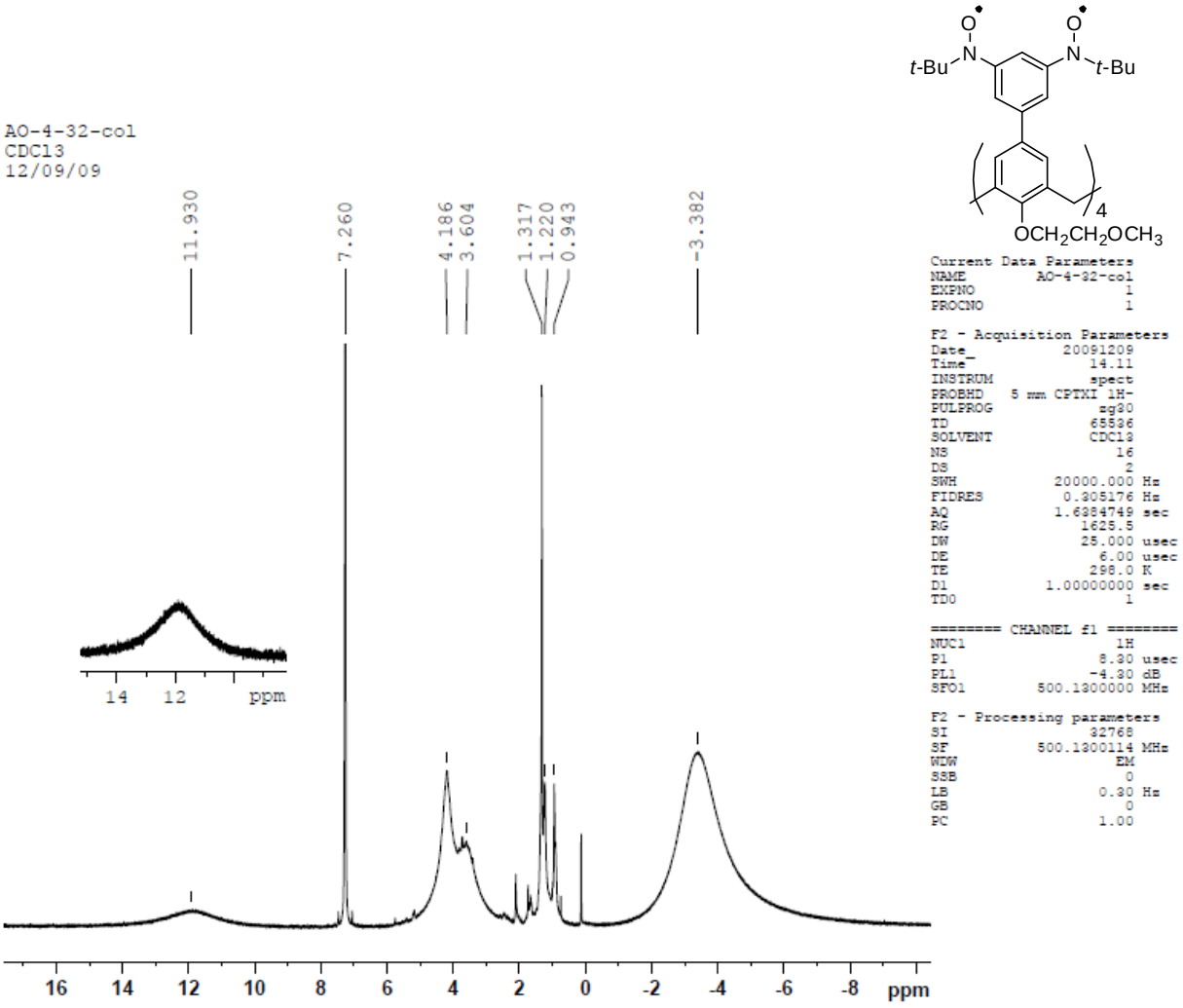


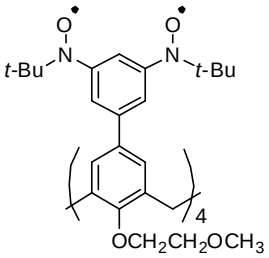


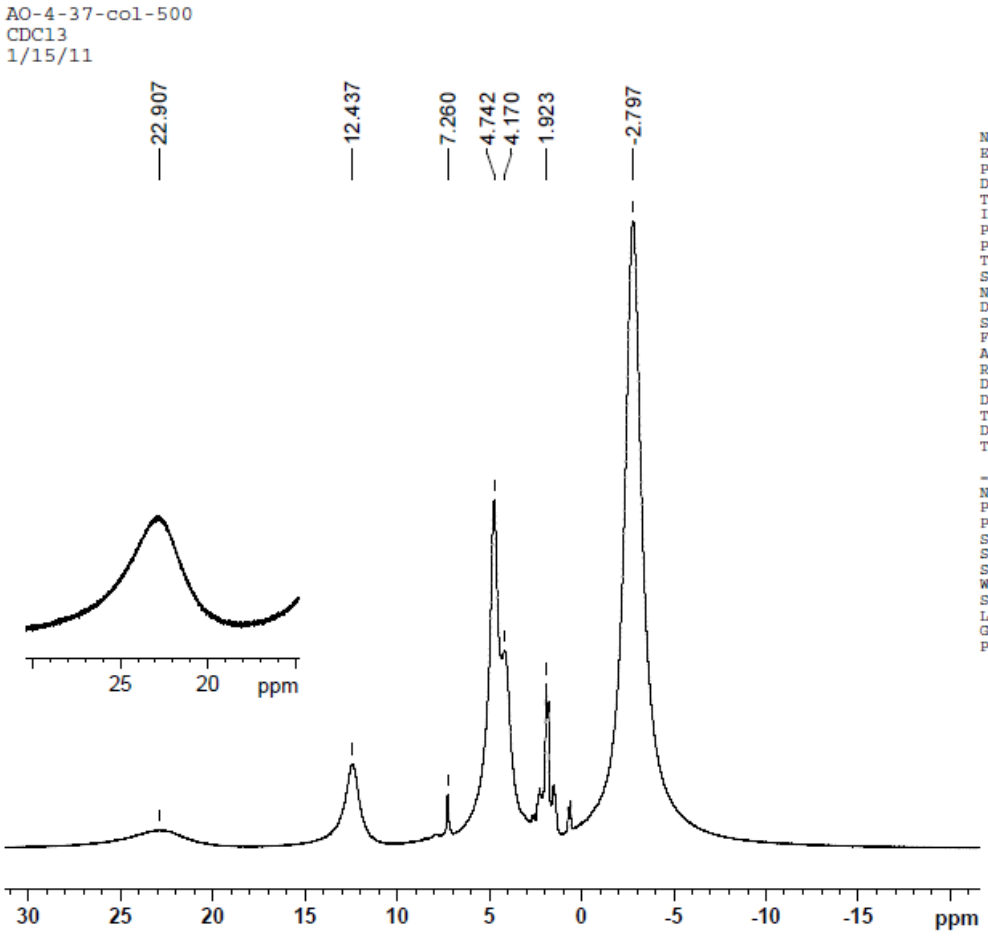
Number of sample scans: 128
Number of background scans: 128
Resolution: 2.000
Sample gain: 1.0
Optical velocity: 0.6329
Aperture: 100.00

^{1}H NMR in chloroform-*d*



^{1}H NMR in chloroform-*d*



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PROCNO                   1
Date_             20110110
Time_                13.52
INSTRUM              spect
PROBHD    5 mm CPTXI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               50125.313 Hz
FIDRES             0.764852 Hz
AQ                 0.6537816 sec
RG                      128
DW                    9.975 usec
DE                    6.00 usec
TE                    298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.30 usec
PL1                  -4.30 dB
SFO1          500.1300000 MHz
SI                    32768
SF            500.1299938 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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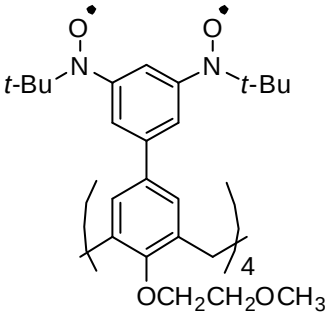
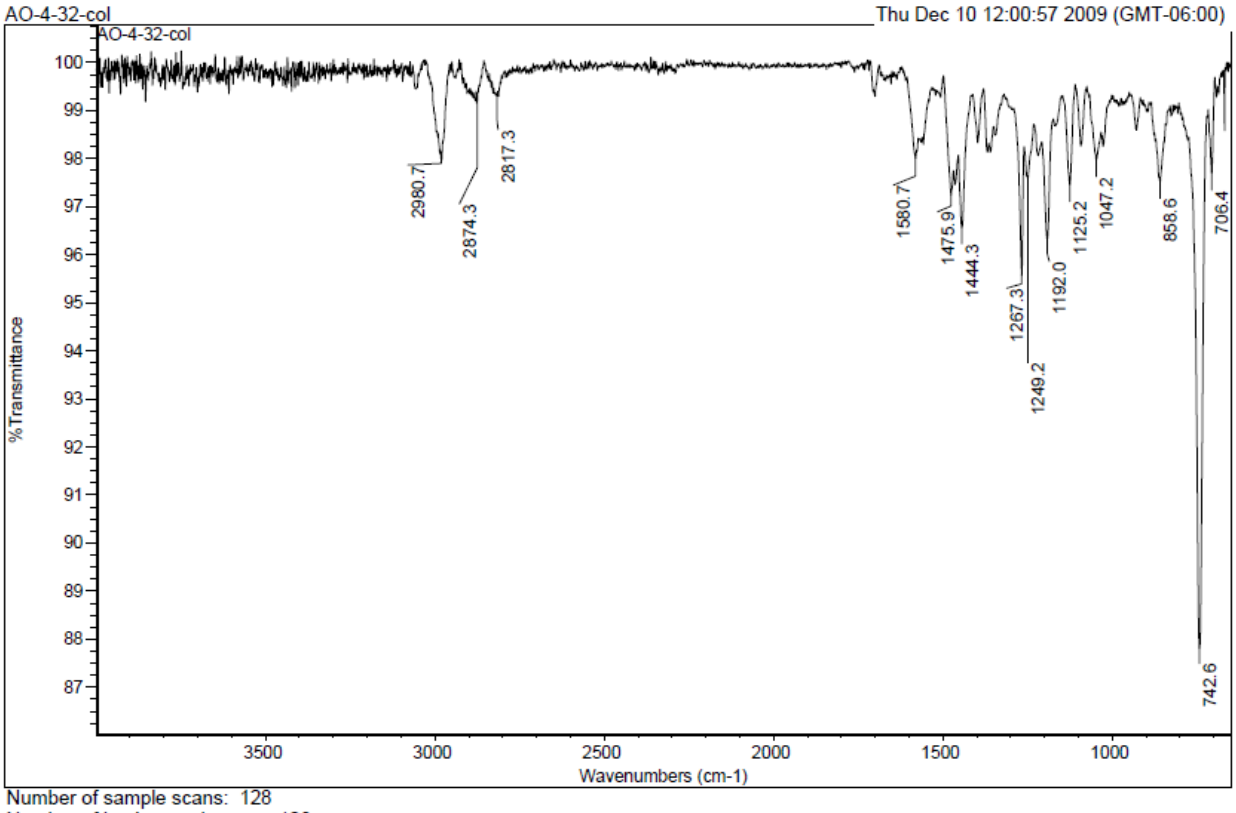
IR





Number of sample scans: 128
Number of background scans: 128
Resolution: 2.000
Sample gain: 1.0
Optical velocity: 0.6329
Aperture: 100.00

9. Supporting references.

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S2. H. Sato, V. Kathirvelu, G. Spagnol, S. Rajca, S. S. Eaton, G. R. Eaton, *J. Phys. Chem. B*, 2008, **112**, 2818–2828.

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10. Outputs of DFT computations for high-spin states of 1a, 2a, and 3a.

Nitroxide tetraradical 1a (^{5}A state) at the UB3LYP/6-31G(d)+ZPVE level (gas phase).

```
Stoichiometry    C48H64N4O8(5)
 Framework group  D2[C2(C.C),C2'(C.C),X(C44H64N4O8)]
 Deg. of freedom    92
 Full point group                 D2
 Largest Abelian subgroup         D2      NOp   4
 Largest concise Abelian subgroup D2      NOp   4
                       Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -2.153095    0.899979    2.581176
    2          6             0       -0.769683    0.998412    2.706513
    3          6             0       -0.091147    1.975709    1.956013
    4          6             0       -0.766686    2.747050    0.997477
    5          6             0       -2.152549    2.628014    0.893023
    6          6             0       -2.869214    1.735394    1.705668
    7          1             0       -2.702603    0.158563    3.144540
    8          1             0       -2.648371    3.211099    0.133223
    9          6             0        0.000000    0.000000    3.565470
   10          1             0        0.712986    0.514574    4.217327
   11          1             0       -0.712986   -0.514574    4.217327
   12          6             0        0.000000    3.608345    0.000000
   13          1             0        0.711593    4.261218    0.516330
   14          1             0       -0.711593    4.261218   -0.516330
   15          6             0        0.769683   -0.998412    2.706513
   16          6             0        2.153095   -0.899979    2.581176
   17          6             0        0.091147   -1.975709    1.956013
   18          6             0        2.869214   -1.735394    1.705668
   19          1             0        2.702603   -0.158563    3.144540
   20          6             0        0.766686   -2.747050    0.997477
   21          6             0        2.152549   -2.628014    0.893023
   22          1             0        2.648371   -3.211099    0.133223
   23          6             0        0.766686    2.747050   -0.997477
   24          6             0        2.152549    2.628014   -0.893023
   25          6             0        0.091147    1.975709   -1.956013
   26          6             0        2.869214    1.735394   -1.705668
   27          1             0        2.648371    3.211099   -0.133223
   28          6             0        0.769683    0.998412   -2.706513
   29          6             0        2.153095    0.899979   -2.581176
   30          1             0        2.702603    0.158563   -3.144540
   31          6             0        0.000000    0.000000   -3.565470
   32          1             0       -0.712986    0.514574   -4.217327
   33          1             0        0.712986   -0.514574   -4.217327
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   35          6             0       -2.153095   -0.899979   -2.581176
   36          6             0       -0.091147   -1.975709   -1.956013
   37          6             0       -2.869214   -1.735394   -1.705668
   38          1             0       -2.702603   -0.158563   -3.144540
   39          6             0       -0.766686   -2.747050   -0.997477
   40          6             0       -2.152549   -2.628014   -0.893023
   41          1             0       -2.648371   -3.211099   -0.133223
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   44          1             0        0.711593   -4.261218   -0.516330
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   47          1             0        1.260902   -4.088120   -2.881356
   48          1             0        1.217362   -2.796153   -4.107244
   49          6             0        1.625240    3.081284    3.128437
   50          1             0        2.716739    3.090856    3.181501
   51          1             0        1.260902    4.088120    2.881356
   52          1             0        1.217362    2.796153    4.107244
   53          8             0        1.276304    2.136464    2.117955
   54          8             0        1.276304   -2.136464   -2.117955
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   57          1             0       -1.260902    4.088120   -2.881356
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   59          6             0       -1.625240   -3.081284    3.128437
   60          1             0       -2.716739   -3.090856    3.181501
   61          1             0       -1.260902   -4.088120    2.881356
   62          1             0       -1.217362   -2.796153    4.107244
   63          8             0       -1.276304   -2.136464    2.117955
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   71          7             0       -4.280995    1.583309    1.656610
   72          7             0       -4.280995   -1.583309   -1.656610
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   74          6             0        5.251118    2.544412   -0.995938
```

```
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   83          1             0        4.202230   -2.795272   -0.941027
   84          1             0        5.269221   -1.396835   -0.867604
   85          6             0        6.668260   -2.127246    1.421660
   86          1             0        6.777772   -2.133974    2.508782
   87          1             0        7.378708   -2.841446    0.991401
   88          1             0        6.918026   -1.127192    1.063306
   89          6             0        4.999687    3.978906   -1.503054
   90          1             0        5.106599    4.022878   -2.592377
   91          1             0        4.011711    4.363513   -1.245440
   92          1             0        5.744997    4.649917   -1.062027
   93          6             0        5.151463    2.434314    0.540072
   94          1             0        5.951810    3.031485    0.992445
   95          1             0        4.202230    2.795272    0.941027
   96          1             0        5.269221    1.396835    0.867604
   97          6             0        6.668260    2.127246   -1.421660
   98          1             0        6.777772    2.133974   -2.508782
   99          1             0        7.378708    2.841446   -0.991401
  100          1             0        6.918026    1.127192   -1.063306
  101          6             0       -4.999687    3.978906    1.503054
  102          1             0       -5.106599    4.022878    2.592377
  103          1             0       -4.011711    4.363513    1.245440
  104          1             0       -5.744997    4.649917    1.062027
  105          6             0       -5.151463    2.434314   -0.540072
  106          1             0       -5.951810    3.031485   -0.992445
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  108          1             0       -5.269221    1.396835   -0.867604
  109          6             0       -6.668260    2.127246    1.421660
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  111          1             0       -7.378708    2.841446    0.991401
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  114          1             0       -6.777772   -2.133974   -2.508782
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  117          6             0       -4.999687   -3.978906   -1.503054
  118          1             0       -5.106599   -4.022878   -2.592377
  119          1             0       -4.011711   -4.363513   -1.245440
  120          1             0       -5.744997   -4.649917   -1.062027
  121          6             0       -5.151463   -2.434314    0.540072
  122          1             0       -4.202230   -2.795272    0.941027
  123          1             0       -5.269221   -1.396835    0.867604
  124          1             0       -5.951810   -3.031485    0.992445
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      0.0652191      0.0358144      0.0328083
 Standard basis: 6-31G(d) (6D, 7F)
SCF Done:  E(UB+HF-LYP) =  -2688.14288501     A.U. after    9 cycles
             Convg  =    0.4669D-08             -V/T =  2.0095
             S**2   =   6.0496
 Annihilation of the first spin contaminant:
 S**2 before annihilation     6.0496,   after     6.0010
The electronic state is 5-A.

Item               Value     Threshold  Converged?
 Maximum Force            0.000006     0.000450     YES
 RMS     Force            0.000001     0.000300     YES
 Maximum Displacement     0.000299     0.001800     YES
 RMS     Displacement     0.000063     0.001200     YES
 Predicted change in Energy=-1.612255D-09
 Optimization completed.
    -- Stationary point found.
```

Nitroxide tetraradical 1a (^{5}A state) at the UB3LYP/6-31G(d,p)+ZPVE level (gas phase).

```
Stoichiometry    C48H64N4O8(5)
 Framework group  D2[C2(C.C),C2'(C.C),X(C44H64N4O8)]
 Deg. of freedom    92
 Full point group                 D2
 Largest Abelian subgroup         D2      NOp   4
 Largest concise Abelian subgroup D2      NOp   4
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -2.153140    0.897919    2.579462
    2          6             0       -0.769981    0.997645    2.705943
    3          6             0       -0.091626    1.975898    1.956477
    4          6             0       -0.766792    2.745715    0.996481
    5          6             0       -2.152105    2.624847    0.889734
    6          6             0       -2.868625    1.732904    1.703220
    7          1             0       -2.703602    0.156827    3.141576
```

8	1	0	-2.647110	3.206714	0.129157
9	6	0	0.000000	0.000000	3.564869
10	1	0	0.712385	0.514949	4.215559
11	1	0	-0.712385	-0.514949	4.215559
12	6	0	0.000000	3.607137	0.000000
13	1	0	0.710915	4.258805	0.516848
14	1	0	-0.710915	4.258805	-0.516848
15	6	0	0.769981	-0.997645	2.705943
16	6	0	2.153140	-0.897919	2.579462
17	6	0	0.091626	-1.975898	1.956477
18	6	0	2.868625	-1.732904	1.703220
19	1	0	2.703602	-0.156827	3.141576
20	6	0	0.766792	-2.745715	0.996481
21	6	0	2.152105	-2.624847	0.889734
22	1	0	2.647110	-3.206714	0.129157
23	6	0	0.766792	2.745715	-0.996481
24	6	0	2.152105	2.624847	-0.889734
25	6	0	0.091626	1.975898	-1.956477
26	6	0	2.868625	1.732904	-1.703220
27	1	0	2.647110	3.206714	-0.129157
28	6	0	0.769981	0.997645	-2.705943
29	6	0	2.153140	0.897919	-2.579462
30	1	0	2.703602	0.156827	-3.141576
31	6	0	0.000000	0.000000	-3.564869
32	1	0	-0.712385	0.514949	-4.215559
33	1	0	0.712385	-0.514949	-4.215559
34	6	0	-0.769981	-0.997645	-2.705943
35	6	0	-2.153140	-0.897919	-2.579462
36	6	0	-0.091626	-1.975898	-1.956477
37	6	0	-2.868625	-1.732904	-1.703220
38	1	0	-2.703602	-0.156827	-3.141576
39	6	0	-0.766792	-2.745715	-0.996481
40	6	0	-2.152105	-2.624847	-0.889734
41	1	0	-2.647110	-3.206714	-0.129157
42	6	0	0.000000	-3.607137	0.000000
43	1	0	-0.710915	-4.258805	0.516848
44	1	0	0.710915	-4.258805	-0.516848
45	6	0	1.620206	-3.084056	-3.133939
46	1	0	2.710793	-3.097526	-3.191551
47	1	0	1.254853	-4.090235	-2.888573
48	1	0	1.211009	-2.798273	-4.111289
49	6	0	1.620206	3.084056	3.133939
50	1	0	2.710793	3.097526	3.191551
51	1	0	1.254853	4.090235	2.888573
52	1	0	1.211009	2.798273	4.111289
53	8	0	1.275435	2.139328	2.120964
54	8	0	1.275435	-2.139328	-2.120964
55	6	0	-1.620206	3.084056	-3.133939
56	1	0	-2.710793	3.097526	-3.191551
57	1	0	-1.254853	4.090235	-2.888573
58	1	0	-1.211009	2.798273	-4.111289
59	6	0	-1.620206	-3.084056	3.133939
60	1	0	-2.710793	-3.097526	3.191551
61	1	0	-1.254853	-4.090235	2.888573
62	1	0	-1.211009	-2.798273	4.111289
63	8	0	-1.275435	-2.139328	2.120964
64	8	0	-1.275435	2.139328	-2.120964
65	8	0	4.789469	-0.575192	2.270593
66	8	0	4.789469	0.575192	-2.270593
67	8	0	-4.789469	0.575192	2.270593
68	8	0	-4.789469	-0.575192	-2.270593
69	7	0	4.280274	-1.582275	1.654474
70	7	0	4.280274	1.582275	-1.654474
71	7	0	-4.280274	1.582275	1.654474
72	7	0	-4.280274	-1.582275	-1.654474
73	6	0	5.247011	-2.535723	0.976928
74	6	0	5.247011	2.535723	-0.976928
75	6	0	-5.247011	2.535723	0.976928
76	6	0	-5.247011	-2.535723	-0.976928
77	6	0	4.999639	-3.975519	1.470382
78	1	0	5.109220	-4.029680	2.557847
79	1	0	4.013099	-4.359789	1.211495
80	1	0	5.745043	-4.639417	1.021617
81	6	0	5.134983	-2.408081	-0.556461
82	1	0	5.918836	-3.014796	-1.022131
83	1	0	4.175832	-2.745392	-0.951240
84	1	0	5.268708	-1.370726	-0.874807
85	6	0	6.665888	-2.121987	1.398161
86	1	0	6.782575	-2.144869	2.483338
87	1	0	7.374035	-2.826859	0.951932
88	1	0	6.909362	-1.116334	1.054683
89	6	0	4.999639	3.975519	-1.470382
90	1	0	5.109220	4.029680	-2.557847
91	1	0	4.013099	4.359789	-1.211495
92	1	0	5.745043	4.639417	-1.021617
93	6	0	5.134983	2.408081	0.556461
94	1	0	5.918836	3.014796	1.022131
95	1	0	4.175832	2.745392	0.951240
96	1	0	5.268708	1.370726	0.874807
97	6	0	6.665888	2.121987	-1.398161
98	1	0	6.782575	2.144869	-2.483338
99	1	0	7.374035	2.826859	-0.951932
100	1	0	6.909362	1.116334	-1.054683

```
  101          6             0       -4.999639    3.975519    1.470382
  102          1             0       -5.109220    4.029680    2.557847
  103          1             0       -4.013099    4.359789    1.211495
  104          1             0       -5.745043    4.639417    1.021617
  105          6             0       -5.134983    2.408081   -0.556461
  106          1             0       -5.918836    3.014796   -1.022131
  107          1             0       -4.175832    2.745392   -0.951240
  108          1             0       -5.268708    1.370726   -0.874807
  109          6             0       -6.665888    2.121987    1.398161
  110          1             0       -6.782575    2.144869    2.483338
  111          1             0       -7.374035    2.826859    0.951932
  112          1             0       -6.909362    1.116334    1.054683
  113          6             0       -6.665888   -2.121987   -1.398161
  114          1             0       -6.782575   -2.144869   -2.483338
  115          1             0       -7.374035   -2.826859   -0.951932
  116          1             0       -6.909362   -1.116334   -1.054683
  117          6             0       -4.999639   -3.975519   -1.470382
  118          1             0       -5.109220   -4.029680   -2.557847
  119          1             0       -4.013099   -4.359789   -1.211495
  120          1             0       -5.745043   -4.639417   -1.021617
  121          6             0       -5.134983   -2.408081    0.556461
  122          1             0       -4.175832   -2.745392    0.951240
  123          1             0       -5.268708   -1.370726    0.874807
  124          1             0       -5.918836   -3.014796    1.022131
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      0.0653867      0.0358702      0.0328678
 Standard basis: 6-31G(d,p) (6D, 7F)
SCF Done:  E(UB+HF-LYP) =  -2688.23369702     A.U. after    7 cycles
            Convg  =    0.4398D-08             -V/T =  2.0094
            S**2   =   6.0499
 Annihilation of the first spin contaminant:
 S**2 before annihilation     6.0499,   after     6.0010
The electronic state is 5-A
    Item               Value     Threshold  Converged?
 Maximum Force            0.000011     0.000450     YES
 RMS     Force            0.000003     0.000300     YES
 Maximum Displacement     0.001264     0.001800     YES
 RMS     Displacement     0.000267     0.001200     YES
 Predicted change in Energy=-2.274002D-08
 Optimization completed.
    -- Stationary point found.
```

Nitroxide tetraradical 2a (^{5}A state) at the UB3LYP/6-31G(d) + ZPVE level (gas phase)

```
Stoichiometry    C72H80N4O8(5)
 Framework group  D2[C2(C.C),C2'(C.C),X(C68H80N4O8)]
 Deg. of freedom   122
 Full point group                 D2
 Largest Abelian subgroup         D2      NOp   4
 Largest concise Abelian subgroup D2      NOp   4
                       Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -2.150773    0.930714    2.652975
    2          6             0       -0.761075    0.999487    2.750531
    3          6             0       -0.086721    1.947778    1.964252
    4          6             0       -0.766520    2.719864    1.006897
    5          6             0       -2.157374    2.613874    0.938792
    6          6             0       -2.877659    1.747142    1.774999
    7          1             0       -2.679320    0.224818    3.285733
    8          1             0       -2.685953    3.187374    0.183467
    9          6             0        0.000000    0.000000    3.612766
   10          1             0        0.717123    0.507969    4.266337
   11          1             0       -0.717123   -0.507969    4.266337
   12          6             0        0.000000    3.571322    0.000000
   13          1             0        0.714622    4.225504    0.510857
   14          1             0       -0.714622    4.225504   -0.510857
   15          6             0        0.761075   -0.999487    2.750531
   16          6             0        2.150773   -0.930714    2.652975
   17          6             0        0.086721   -1.947778    1.964252
   18          6             0        2.877659   -1.747142    1.774999
   19          1             0        2.679320   -0.224818    3.285733
   20          6             0        0.766520   -2.719864    1.006897
   21          6             0        2.157374   -2.613874    0.938792
   22          1             0        2.685953   -3.187374    0.183467
   23          6             0        0.766520    2.719864   -1.006897
   24          6             0        2.157374    2.613874   -0.938792
   25          6             0        0.086721    1.947778   -1.964252
   26          6             0        2.877659    1.747142   -1.774999
   27          1             0        2.685953    3.187374   -0.183467
   28          6             0        0.761075    0.999487   -2.750531
   29          6             0        2.150773    0.930714   -2.652975
   30          1             0        2.679320    0.224818   -3.285733
   31          6             0        0.000000    0.000000   -3.612766
   32          1             0       -0.717123    0.507969   -4.266337
   33          1             0        0.717123   -0.507969   -4.266337
   34          6             0       -0.761075   -0.999487   -2.750531
```

35	6	0	-2.150773	-0.930714	-2.652975
36	6	0	-0.086721	-1.947778	-1.964252
37	6	0	-2.877659	-1.747142	-1.774999
38	1	0	-2.679320	-0.224818	-3.285733
39	6	0	-0.766520	-2.719864	-1.006897
40	6	0	-2.157374	-2.613874	-0.938792
41	1	0	-2.685953	-3.187374	-0.183467
42	6	0	0.000000	-3.571322	0.000000
43	1	0	-0.714622	-4.225504	0.510857
44	1	0	0.714622	-4.225504	-0.510857
45	6	0	-4.355523	1.666066	1.721760
46	6	0	-5.147221	2.796322	1.464081
47	6	0	-5.032987	0.452793	1.948654
48	6	0	-6.537075	2.735019	1.443375
49	1	0	-4.668818	3.759106	1.307316
50	6	0	-6.416132	0.375561	1.943847
51	1	0	-4.458264	-0.456016	2.100370
52	6	0	-7.202013	1.518952	1.693488
53	1	0	-7.082135	3.648075	1.255402
54	1	0	-6.919957	-0.565346	2.118868
55	6	0	-4.355523	-1.666066	-1.721760
56	6	0	-5.147221	-2.796322	-1.464081
57	6	0	-5.032987	-0.452793	-1.948654
58	6	0	-6.537075	-2.735019	-1.443375
59	1	0	-4.668818	-3.759106	-1.307316
60	6	0	-6.416132	-0.375561	-1.943847
61	1	0	-4.458264	0.456016	-2.100370
62	6	0	-7.202013	-1.518952	-1.693488
63	1	0	-7.082135	-3.648075	-1.255402
64	1	0	-6.919957	0.565346	-2.118868
65	6	0	4.355523	1.666066	-1.721760
66	6	0	5.032987	0.452793	-1.948654
67	6	0	5.147221	2.796322	-1.464081
68	6	0	6.537075	2.735019	-1.443375
69	1	0	4.458264	-0.456016	-2.100370
70	6	0	6.416132	0.375561	-1.943847
71	1	0	4.668818	3.759106	-1.307316
72	6	0	7.202013	1.518952	-1.693488
73	1	0	7.082135	3.648075	-1.255402
74	1	0	6.919957	-0.565346	-2.118868
75	6	0	4.355523	-1.666066	1.721760
76	6	0	5.147221	-2.796322	1.464081
77	6	0	5.032987	-0.452793	1.948654
78	6	0	6.537075	-2.735019	1.443375
79	1	0	4.668818	-3.759106	1.307316
80	6	0	6.416132	-0.375561	1.943847
81	1	0	4.458264	0.456016	2.100370
82	6	0	7.202013	-1.518952	1.693488
83	1	0	7.082135	-3.648075	1.255402
84	1	0	6.919957	0.565346	2.118868
85	6	0	1.669174	-3.059986	-3.066721
86	1	0	2.762109	-3.079456	-3.076652
87	1	0	1.290619	-4.058315	-2.808453
88	1	0	1.301690	-2.799027	-4.068356
89	6	0	1.669174	3.059986	3.066721
90	1	0	2.762109	3.079456	3.076652
91	1	0	1.290619	4.058315	2.808453
92	1	0	1.301690	2.799027	4.068356
93	8	0	1.287756	2.086629	2.096948
94	8	0	1.287756	-2.086629	-2.096948
95	6	0	-1.669174	3.059986	-3.066721
96	1	0	-2.762109	3.079456	-3.076652
97	1	0	-1.290619	4.058315	-2.808453
98	1	0	-1.301690	2.799027	-4.068356
99	6	0	-1.669174	-3.059986	3.066721
100	1	0	-2.762109	-3.079456	3.076652
101	1	0	-1.290619	-4.058315	2.808453
102	1	0	-1.301690	-2.799027	4.068356
103	8	0	-1.287756	-2.086629	2.096948
104	8	0	-1.287756	2.086629	-2.096948
105	7	0	8.610862	-1.364280	1.728885
106	7	0	8.610862	1.364280	-1.728885
107	8	0	9.070756	-0.233977	2.132246
108	8	0	9.070756	0.233977	-2.132246
109	6	0	9.626749	-2.408190	1.303934
110	6	0	9.615353	-3.588286	2.298285
111	6	0	9.356259	-2.840791	-0.151068
112	6	0	11.014132	-1.750697	1.362814
113	1	0	9.817908	-3.227996	3.312396
114	1	0	8.671545	-4.135956	2.318678
115	1	0	10.405046	-4.296954	2.025220
116	1	0	9.331099	-1.963776	-0.806425
117	1	0	10.167253	-3.497433	-0.485235
118	1	0	8.418602	-3.385783	-0.274929
119	1	0	11.758319	-2.497339	1.065483
120	1	0	11.081537	-0.901997	0.679422
121	1	0	11.250649	-1.396886	2.367946
122	6	0	9.626749	2.408190	-1.303934
123	6	0	9.615353	3.588286	-2.298285
124	6	0	9.356259	2.840791	0.151068
125	6	0	11.014132	1.750697	-1.362814
126	1	0	9.817908	3.227996	-3.312396
127	1	0	8.671545	4.135956	-2.318678

```
  128          1             0       10.405046    4.296954   -2.025220
  129          1             0        9.331099    1.963776    0.806425
  130          1             0       10.167253    3.497433    0.485235
  131          1             0        8.418602    3.385783    0.274929
  132          1             0       11.758319    2.497339   -1.065483
  133          1             0       11.081537    0.901997   -0.679422
  134          1             0       11.250649    1.396886   -2.367946
  135          7             0       -8.610862   -1.364280   -1.728885
  136          7             0       -8.610862    1.364280    1.728885
  137          6             0       -9.626749    2.408190    1.303934
  138          6             0       -9.615353    3.588286    2.298285
  139          6             0       -9.356259    2.840791   -0.151068
  140          6             0      -11.014132    1.750697    1.362814
  141          1             0       -9.817908    3.227996    3.312396
  142          1             0       -8.671545    4.135956    2.318678
  143          1             0      -10.405046    4.296954    2.025220
  144          1             0       -9.331099    1.963776   -0.806425
  145          1             0      -10.167253    3.497433   -0.485235
  146          1             0       -8.418602    3.385783   -0.274929
  147          1             0      -11.758319    2.497339    1.065483
  148          1             0      -11.081537    0.901997    0.679422
  149          1             0      -11.250649    1.396886    2.367946
  150          6             0       -9.626749   -2.408190   -1.303934
  151          6             0       -9.615353   -3.588286   -2.298285
  152          6             0       -9.356259   -2.840791    0.151068
  153          6             0      -11.014132   -1.750697   -1.362814
  154          1             0       -9.817908   -3.227996   -3.312396
  155          1             0       -8.671545   -4.135956   -2.318678
  156          1             0      -10.405046   -4.296954   -2.025220
  157          1             0       -9.331099   -1.963776    0.806425
  158          1             0      -10.167253   -3.497433    0.485235
  159          1             0       -8.418602   -3.385783    0.274929
  160          1             0      -11.758319   -2.497339   -1.065483
  161          1             0      -11.081537   -0.901997   -0.679422
  162          1             0      -11.250649   -1.396886   -2.367946
  163          8             0       -9.070756   -0.233977   -2.132246
  164          8             0       -9.070756    0.233977    2.132246
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      0.0521620      0.0105024      0.0102800
 Standard basis: 6-31G(d) (6D, 7F)
SCF Done:  E(UB+HF-LYP) =  -3612.37501081     A.U. after    7 cycles
            Convg  =    0.1788D-08             -V/T =  2.0096
            S**2   =   6.0538
 Annihilation of the first spin contaminant:
 S**2 before annihilation     6.0538,   after     6.0012
        Item               Value     Threshold  Converged?
 Maximum Force            0.000002     0.000450     YES
 RMS     Force            0.000001     0.000300     YES
 Maximum Displacement     0.015619     0.001800     NO
 RMS     Displacement     0.001728     0.001200     NO
 Predicted change in Energy=-4.823541D-07
 Optimization completed on the basis of negligible forces.
    -- Stationary point found.
```

Nitroxide tetraradical 2a (^{5}A state) at the UB3LYP/6-31G(d,p) level (gas phase)

```
Stoichiometry    C72H80N4O8(5)
 Framework group  D2[C2(C.C),C2'(C.C),X(C68H80N4O8)]
 Deg. of freedom   122
 Full point group                 D2
 Largest Abelian subgroup         D2      NOp   4
 Largest concise Abelian subgroup D2      NOp   4
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -2.150995    0.926701    2.652322
    2          6             0       -0.761697    0.997908    2.751722
    3          6             0       -0.087808    1.946645    1.965662
    4          6             0       -0.767363    2.715734    1.005838
    5          6             0       -2.157780    2.606641    0.934793
    6          6             0       -2.877608    1.740625    1.771980
    7          1             0       -2.678850    0.221086    3.284973
    8          1             0       -2.685383    3.177037    0.177317
    9          6             0        0.000000    0.000000    3.614489
   10          1             0        0.716218    0.508705    4.266955
   11          1             0       -0.716218   -0.508705    4.266955
   12          6             0        0.000000    3.566961    0.000000
   13          1             0        0.713570    4.219995    0.511831
   14          1             0       -0.713570    4.219995   -0.511831
   15          6             0        0.761697   -0.997908    2.751722
   16          6             0        2.150995   -0.926701    2.652322
   17          6             0        0.087808   -1.946645    1.965662
   18          6             0        2.877608   -1.740625    1.771980
   19          1             0        2.678850   -0.221086    3.284973
   20          6             0        0.767363   -2.715734    1.005838
   21          6             0        2.157780   -2.606641    0.934793
   22          1             0        2.685383   -3.177037    0.177317
   23          6             0        0.767363    2.715734   -1.005838
```

24	6	0	2.157780	2.606641	-0.934793
25	6	0	0.087808	1.946645	-1.965662
26	6	0	2.877608	1.740625	-1.771980
27	1	0	2.685383	3.177037	-0.177317
28	6	0	0.761697	0.997908	-2.751722
29	6	0	2.150995	0.926701	-2.652322
30	1	0	2.678850	0.221086	-3.284973
31	6	0	0.000000	0.000000	-3.614489
32	1	0	-0.716218	0.508705	-4.266955
33	1	0	0.716218	-0.508705	-4.266955
34	6	0	-0.761697	-0.997908	-2.751722
35	6	0	-2.150995	-0.926701	-2.652322
36	6	0	-0.087808	-1.946645	-1.965662
37	6	0	-2.877608	-1.740625	-1.771980
38	1	0	-2.678850	-0.221086	-3.284973
39	6	0	-0.767363	-2.715734	-1.005838
40	6	0	-2.157780	-2.606641	-0.934793
41	1	0	-2.685383	-3.177037	-0.177317
42	6	0	0.000000	-3.566961	0.000000
43	1	0	-0.713570	-4.219995	0.511831
44	1	0	0.713570	-4.219995	-0.511831
45	6	0	-4.355280	1.657119	1.717663
46	6	0	-5.148140	2.785327	1.455175
47	6	0	-5.030647	0.443619	1.949136
48	6	0	-6.537632	2.721971	1.434708
49	1	0	-4.670877	3.747278	1.294179
50	6	0	-6.413395	0.364485	1.945298
51	1	0	-4.454494	-0.462985	2.104250
52	6	0	-7.200321	1.506026	1.690827
53	1	0	-7.084542	3.632256	1.241644
54	1	0	-6.917764	-0.574906	2.124452
55	6	0	-4.355280	-1.657119	-1.717663
56	6	0	-5.148140	-2.785327	-1.455175
57	6	0	-5.030647	-0.443619	-1.949136
58	6	0	-6.537632	-2.721971	-1.434708
59	1	0	-4.670877	-3.747278	-1.294179
60	6	0	-6.413395	-0.364485	-1.945298
61	1	0	-4.454494	0.462985	-2.104250
62	6	0	-7.200321	-1.506026	-1.690827
63	1	0	-7.084542	-3.632256	-1.241644
64	1	0	-6.917764	0.574906	-2.124452
65	6	0	4.355280	1.657119	-1.717663
66	6	0	5.030647	0.443619	-1.949136
67	6	0	5.148140	2.785327	-1.455175
68	6	0	6.537632	2.721971	-1.434708
69	1	0	4.454494	-0.462985	-2.104250
70	6	0	6.413395	0.364485	-1.945298
71	1	0	4.670877	3.747278	-1.294179
72	6	0	7.200321	1.506026	-1.690827
73	1	0	7.084542	3.632256	-1.241644
74	1	0	6.917764	-0.574906	-2.124452
75	6	0	4.355280	-1.657119	1.717663
76	6	0	5.148140	-2.785327	1.455175
77	6	0	5.030647	-0.443619	1.949136
78	6	0	6.537632	-2.721971	1.434708
79	1	0	4.670877	-3.747278	1.294179
80	6	0	6.413395	-0.364485	1.945298
81	1	0	4.454494	0.462985	2.104250
82	6	0	7.200321	-1.506026	1.690827
83	1	0	7.084542	-3.632256	1.241644
84	1	0	6.917764	0.574906	2.124452
85	6	0	1.663759	-3.063052	-3.071759
86	1	0	2.755895	-3.087166	-3.085360
87	1	0	1.283552	-4.060379	-2.814632
88	1	0	1.295777	-2.802307	-4.072592
89	6	0	1.663759	3.063052	3.071759
90	1	0	2.755895	3.087166	3.085360
91	1	0	1.283552	4.060379	2.814632
92	1	0	1.295777	2.802307	4.072592
93	8	0	1.286231	2.088696	2.100626
94	8	0	1.286231	-2.088696	-2.100626
95	6	0	-1.663759	3.063052	-3.071759
96	1	0	-2.755895	3.087166	-3.085360
97	1	0	-1.283552	4.060379	-2.814632
98	1	0	-1.295777	2.802307	-4.072592
99	6	0	-1.663759	-3.063052	3.071759
100	1	0	-2.755895	-3.087166	3.085360
101	1	0	-1.283552	-4.060379	2.814632
102	1	0	-1.295777	-2.802307	4.072592
103	8	0	-1.286231	-2.088696	2.100626
104	8	0	-1.286231	2.088696	-2.100626
105	7	0	8.608754	-1.350129	1.727333
106	7	0	8.608754	1.350129	-1.727333
107	8	0	9.068001	-0.217819	2.125587
108	8	0	9.068001	0.217819	-2.125587
109	6	0	9.625421	-2.397155	1.310530
110	6	0	9.602569	-3.576295	2.305365
111	6	0	9.363401	-2.829669	-0.145772
112	6	0	11.013126	-1.742507	1.379707
113	1	0	9.799424	-3.216481	3.319584
114	1	0	8.657426	-4.119624	2.319441
115	1	0	10.390622	-4.287352	2.038288
116	1	0	9.342892	-1.953439	-0.800690

```
  117          1             0       10.174863   -3.486793   -0.474212
  118          1             0        8.426840   -3.373331   -0.274574
  119          1             0       11.757595   -2.490445    1.090614
  120          1             0       11.086985   -0.895847    0.696196
  121          1             0       11.240324   -1.386470    2.385182
  122          6             0        9.625421    2.397155   -1.310530
  123          6             0        9.602569    3.576295   -2.305365
  124          6             0        9.363401    2.829669    0.145772
  125          6             0       11.013126    1.742507   -1.379707
  126          1             0        9.799424    3.216481   -3.319584
  127          1             0        8.657426    4.119624   -2.319441
  128          1             0       10.390622    4.287352   -2.038288
  129          1             0        9.342892    1.953439    0.800690
  130          1             0       10.174863    3.486793    0.474212
  131          1             0        8.426840    3.373331    0.274574
  132          1             0       11.757595    2.490445   -1.090614
  133          1             0       11.086985    0.895847   -0.696196
  134          1             0       11.240324    1.386470   -2.385182
  135          7             0       -8.608754   -1.350129   -1.727333
  136          7             0       -8.608754    1.350129    1.727333
  137          6             0       -9.625421    2.397155    1.310530
  138          6             0       -9.602569    3.576295    2.305365
  139          6             0       -9.363401    2.829669   -0.145772
  140          6             0      -11.013126    1.742507    1.379707
  141          1             0       -9.799424    3.216481    3.319584
  142          1             0       -8.657426    4.119624    2.319441
  143          1             0      -10.390622    4.287352    2.038288
  144          1             0       -9.342892    1.953439   -0.800690
  145          1             0      -10.174863    3.486793   -0.474212
  146          1             0       -8.426840    3.373331   -0.274574
  147          1             0      -11.757595    2.490445    1.090614
  148          1             0      -11.086985    0.895847    0.696196
  149          1             0      -11.240324    1.386470    2.385182
  150          6             0       -9.625421   -2.397155   -1.310530
  151          6             0       -9.602569   -3.576295   -2.305365
  152          6             0       -9.363401   -2.829669    0.145772
  153          6             0      -11.013126   -1.742507   -1.379707
  154          1             0       -9.799424   -3.216481   -3.319584
  155          1             0       -8.657426   -4.119624   -2.319441
  156          1             0      -10.390622   -4.287352   -2.038288
  157          1             0       -9.342892   -1.953439    0.800690
  158          1             0      -10.174863   -3.486793    0.474212
  159          1             0       -8.426840   -3.373331    0.274574
  160          1             0      -11.757595   -2.490445   -1.090614
  161          1             0      -11.086985   -0.895847   -0.696196
  162          1             0      -11.240324   -1.386470   -2.385182
  163          8             0       -9.068001   -0.217819   -2.125587
  164          8             0       -9.068001    0.217819    2.125587
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      0.0523158      0.0105060      0.0102906
 Standard basis: 6-31G(d,p) (6D, 7F)
SCF Done:  E(UB+HF-LYP) =  -3612.49077302     A.U. after    6 cycles
             Convg  =    0.4729D-08             -V/T =  2.0096
             S**2   =   6.0539
 Annihilation of the first spin contaminant:
 S**2 before annihilation     6.0539,   after     6.0012
The electronic state is 5-A
Item               Value     Threshold  Converged?
 Maximum Force            0.000014     0.000450     YES
 RMS     Force            0.000003     0.000300     YES
 Maximum Displacement     0.000782     0.001800     YES
 RMS     Displacement     0.000143     0.001200     YES
 Predicted change in Energy=-5.440062D-09
 Optimization completed.
    -- Stationary point found.
```

Nitroxide tetraradical 2a (^{5}A state) at the UB3LYP/6-31G(d)/UA0-PCM+ZPVE level (THF, Gaussian 03 default).

```
Stoichiometry    C72H80N4O8(5)
 Framework group  D2[C2(C.C),C2'(C.C),X(C68H80N4O8)]
 Deg. of freedom   122
 Full point group                 D2
 Largest Abelian subgroup         D2      NOp   4
 Largest concise Abelian subgroup D2      NOp   4
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic             Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -2.150049    0.939329    2.668190
    2          6             0       -0.759293    1.000278    2.756293
    3          6             0       -0.083744    1.941689    1.962046
    4          6             0       -0.765935    2.716807    1.007985
    5          6             0       -2.158093    2.618509    0.947775
    6          6             0       -2.877400    1.755919    1.789887
    7          1             0       -2.677181    0.239815    3.310161
    8          1             0       -2.687684    3.195705    0.195911
```

9	6	0	0.000000	0.000000	3.619010
10	1	0	0.718148	0.507268	4.272395
11	1	0	-0.718148	-0.507268	4.272395
12	6	0	0.000000	3.567723	0.000000
13	1	0	0.714777	4.221840	0.511094
14	1	0	-0.714777	4.221840	-0.511094
15	6	0	0.759293	-1.000278	2.756293
16	6	0	2.150049	-0.939329	2.668190
17	6	0	0.083744	-1.941689	1.962046
18	6	0	2.877400	-1.755919	1.789887
19	1	0	2.677181	-0.239815	3.310161
20	6	0	0.765935	-2.716807	1.007985
21	6	0	2.158093	-2.618509	0.947775
22	1	0	2.687684	-3.195705	0.195911
23	6	0	0.765935	2.716807	-1.007985
24	6	0	2.158093	2.618509	-0.947775
25	6	0	0.083744	1.941689	-1.962046
26	6	0	2.877400	1.755919	-1.789887
27	1	0	2.687684	3.195705	-0.195911
28	6	0	0.759293	1.000278	-2.756293
29	6	0	2.150049	0.939329	-2.668190
30	1	0	2.677181	0.239815	-3.310161
31	6	0	0.000000	0.000000	-3.619010
32	1	0	-0.718148	0.507268	-4.272395
33	1	0	0.718148	-0.507268	-4.272395
34	6	0	-0.759293	-1.000278	-2.756293
35	6	0	-2.150049	-0.939329	-2.668190
36	6	0	-0.083744	-1.941689	-1.962046
37	6	0	-2.877400	-1.755919	-1.789887
38	1	0	-2.677181	-0.239815	-3.310161
39	6	0	-0.765935	-2.716807	-1.007985
40	6	0	-2.158093	-2.618509	-0.947775
41	1	0	-2.687684	-3.195705	-0.195911
42	6	0	0.000000	-3.567723	0.000000
43	1	0	-0.714777	-4.221840	0.511094
44	1	0	0.714777	-4.221840	-0.511094
45	6	0	-4.356059	1.677716	1.745142
46	6	0	-5.149308	2.805524	1.476858
47	6	0	-5.032276	0.467810	1.995776
48	6	0	-6.539905	2.745676	1.473391
49	1	0	-4.673880	3.767599	1.298301
50	6	0	-6.415802	0.393019	2.009913
51	1	0	-4.457505	-0.439874	2.153019
52	6	0	-7.202504	1.534664	1.753420
53	1	0	-7.083926	3.658959	1.279610
54	1	0	-6.915698	-0.546784	2.204589
55	6	0	-4.356059	-1.677716	-1.745142
56	6	0	-5.149308	-2.805524	-1.476858
57	6	0	-5.032276	-0.467810	-1.995776
58	6	0	-6.539905	-2.745676	-1.473391
59	1	0	-4.673880	-3.767599	-1.298301
60	6	0	-6.415802	-0.393019	-2.009913
61	1	0	-4.457505	0.439874	-2.153019
62	6	0	-7.202504	-1.534664	-1.753420
63	1	0	-7.083926	-3.658959	-1.279610
64	1	0	-6.915698	0.546784	-2.204589
65	6	0	4.356059	1.677716	-1.745142
66	6	0	5.032276	0.467810	-1.995776
67	6	0	5.149308	2.805524	-1.476858
68	6	0	6.539905	2.745676	-1.473391
69	1	0	4.457505	-0.439874	-2.153019
70	6	0	6.415802	0.393019	-2.009913
71	1	0	4.673880	3.767599	-1.298301
72	6	0	7.202504	1.534664	-1.753420
73	1	0	7.083926	3.658959	-1.279610
74	1	0	6.915698	-0.546784	-2.204589
75	6	0	4.356059	-1.677716	1.745142
76	6	0	5.149308	-2.805524	1.476858
77	6	0	5.032276	-0.467810	1.995776
78	6	0	6.539905	-2.745676	1.473391
79	1	0	4.673880	-3.767599	1.298301
80	6	0	6.415802	-0.393019	2.009913
81	1	0	4.457505	0.439874	2.153019
82	6	0	7.202504	-1.534664	1.753420
83	1	0	7.083926	-3.658959	1.279610
84	1	0	6.915698	0.546784	2.204589
85	6	0	1.691651	-3.040619	-3.050472
86	1	0	2.784593	-3.050286	-3.048469
87	1	0	1.319655	-4.041968	-2.795421
88	1	0	1.333182	-2.780356	-4.055296
89	6	0	1.691651	3.040619	3.050472
90	1	0	2.784593	3.050286	3.048469
91	1	0	1.319655	4.041968	2.795421
92	1	0	1.333182	2.780356	4.055296
93	8	0	1.290962	2.070101	2.082511
94	8	0	1.290962	-2.070101	-2.082511
95	6	0	-1.691651	3.040619	-3.050472
96	1	0	-2.784593	3.050286	-3.048469
97	1	0	-1.319655	4.041968	-2.795421
98	1	0	-1.333182	2.780356	-4.055296
99	6	0	-1.691651	-3.040619	3.050472
100	1	0	-2.784593	-3.050286	3.048469
101	1	0	-1.319655	-4.041968	2.795421

```
 102          1             0       -1.333182   -2.780356    4.055296
 103          8             0       -1.290962   -2.070101    2.082511
 104          8             0       -1.290962    2.070101   -2.082511
 105          7             0        8.611510   -1.387262    1.821122
 106          7             0        8.611510    1.387262   -1.821122
 107          8             0        9.065565   -0.290786    2.319338
 108          8             0        9.065565    0.290786   -2.319338
 109          6             0        9.632929   -2.395715    1.326891
 110          6             0        9.649947   -3.625125    2.259218
 111          6             0        9.341635   -2.761853   -0.141899
 112          6             0       11.013782   -1.725778    1.396957
 113          1             0        9.852075   -3.314176    3.289831
 114          1             0        8.717158   -4.191997    2.252759
 115          1             0       10.451776   -4.302258    1.944914
 116          1             0        9.305608   -1.858598   -0.760786
 117          1             0       10.149566   -3.401211   -0.514525
 118          1             0        8.404048   -3.304707   -0.274906
 119          1             0       11.757880   -2.440320    1.029830
 120          1             0       11.055137   -0.828899    0.774976
 121          1             0       11.273914   -1.442639    2.418797
 122          6             0        9.632929    2.395715   -1.326891
 123          6             0        9.649947    3.625125   -2.259218
 124          6             0        9.341635    2.761853    0.141899
 125          6             0       11.013782    1.725778   -1.396957
 126          1             0        9.852075    3.314176   -3.289831
 127          1             0        8.717158    4.191997   -2.252759
 128          1             0       10.451776    4.302258   -1.944914
 129          1             0        9.305608    1.858598    0.760786
 130          1             0       10.149566    3.401211    0.514525
 131          1             0        8.404048    3.304707    0.274906
 132          1             0       11.757880    2.440320   -1.029830
 133          1             0       11.055137    0.828899   -0.774976
 134          1             0       11.273914    1.442639   -2.418797
 135          7             0       -8.611510   -1.387262   -1.821122
 136          7             0       -8.611510    1.387262    1.821122
 137          6             0       -9.632929    2.395715    1.326891
 138          6             0       -9.649947    3.625125    2.259218
 139          6             0       -9.341635    2.761853   -0.141899
 140          6             0      -11.013782    1.725778    1.396957
 141          1             0       -9.852075    3.314176    3.289831
 142          1             0       -8.717158    4.191997    2.252759
 143          1             0      -10.451776    4.302258    1.944914
 144          1             0       -9.305608    1.858598   -0.760786
 145          1             0      -10.149566    3.401211   -0.514525
 146          1             0       -8.404048    3.304707   -0.274906
 147          1             0      -11.757880    2.440320    1.029830
 148          1             0      -11.055137    0.828899    0.774976
 149          1             0      -11.273914    1.442639    2.418797
 150          6             0       -9.632929   -2.395715   -1.326891
 151          6             0       -9.649947   -3.625125   -2.259218
 152          6             0       -9.341635   -2.761853    0.141899
 153          6             0      -11.013782   -1.725778   -1.396957
 154          1             0       -9.852075   -3.314176   -3.289831
 155          1             0       -8.717158   -4.191997   -2.252759
 156          1             0      -10.451776   -4.302258   -1.944914
 157          1             0       -9.305608   -1.858598    0.760786
 158          1             0      -10.149566   -3.401211    0.514525
 159          1             0       -8.404048   -3.304707    0.274906
 160          1             0      -11.757880   -2.440320   -1.029830
 161          1             0      -11.055137   -0.828899   -0.774976
 162          1             0      -11.273914   -1.442639   -2.418797
 163          8             0       -9.065565   -0.290786   -2.319338
 164          8             0       -9.065565    0.290786    2.319338
 ---------------------------------------------------------------------
 Rotational constants (GHZ): 0.0516306      0.0104710      0.0102760
 Standard basis: 6-31G(d) (6D, 7F)
---------------------------------------------------------------------
 Polarizable Continuum Model (PCM)
 =================================
 Model                : PCM.
 Atomic radii         : UA0 (Simple United Atom Topological Model).
 Polarization charges : Total charges.
 Charge compensation  : None.
 Solution method      : Matrix inversion.
 Cavity               : GePol (RMin=0.200 OFac=0.890).
                        Default sphere list used, NSphG=   84.
                        Tesserae with average area of 0.200 Ang**2.
 1st derivatives      : Analytical V*U(x)*V algorithm (CHGder, D1EAlg=0).
                        Cavity 1st derivative terms included.
 Solvent              : THF, Eps     =   7.580000
                                Eps(inf)=   1.971000
                                RSolv   =   2.560000 Ang.
 ---------------------------------------------------------------------
---------------------------------------------------------------------
 After PCM corrections, the SCF energy is  -3612.39443871     a.u.
 ---------------------------------------------------------------------
 Annihilation of the first spin contaminant:
 S**2 before annihilation     6.0544,   after     6.0012
 The electronic state is 5-A.
        Item               Value     Threshold  Converged?
 Maximum Force            0.000086     0.000450     YES
 RMS     Force            0.000016     0.000300     YES
 Maximum Displacement     0.001477     0.001800     YES
```

```
RMS     Displacement     0.000337     0.001200     YES
Predicted change in Energy=-1.420195D-04
Optimization completed.
   -- Stationary point found.
```

Nitroxide octaradical 3a (^{9}A state) at the UB3LYP/6-31G(d)+ZPVE level (gas phase).

```
Stoichiometry    C88H112N8O12(9)
 Framework group  D2[C2(C.C),C2'(C.C),X(C84H112N8O12)]
 Deg. of freedom   164
 Full point group                 D2
 Largest Abelian subgroup         D2      NOp   4
 Largest concise Abelian subgroup D2      NOp   4
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.140019	1.051079	2.813377
2	6	0	-0.745425	1.019726	2.812771
3	6	0	-0.062274	1.904209	1.962706
4	6	0	-0.751634	2.701171	1.033887
5	6	0	-2.147711	2.682509	1.053961
6	6	0	-2.868431	1.894464	1.964006
7	1	0	-2.665094	0.406870	3.512261
8	1	0	-2.683658	3.281190	0.323971
9	6	0	0.000000	0.000000	3.663819
10	1	0	0.726323	0.492628	4.320091
11	1	0	-0.726323	-0.492628	4.320091
12	6	0	0.000000	3.531862	0.000000
13	1	0	0.723386	4.189287	0.494778
14	1	0	-0.723386	4.189287	-0.494778
15	6	0	0.745425	-1.019726	2.812771
16	6	0	2.140019	-1.051079	2.813377
17	6	0	0.062274	-1.904209	1.962706
18	6	0	2.868431	-1.894464	1.964006
19	1	0	2.665094	-0.406870	3.512261
20	6	0	0.751634	-2.701171	1.033887
21	6	0	2.147711	-2.682509	1.053961
22	1	0	2.683658	-3.281190	0.323971
23	6	0	0.751634	2.701171	-1.033887
24	6	0	2.147711	2.682509	-1.053961
25	6	0	0.062274	1.904209	-1.962706
26	6	0	2.868431	1.894464	-1.964006
27	1	0	2.683658	3.281190	-0.323971
28	6	0	0.745425	1.019726	-2.812771
29	6	0	2.140019	1.051079	-2.813377
30	1	0	2.665094	0.406870	-3.512261
31	6	0	0.000000	0.000000	-3.663819
32	1	0	-0.726323	0.492628	-4.320091
33	1	0	0.726323	-0.492628	-4.320091
34	6	0	-0.745425	-1.019726	-2.812771
35	6	0	-2.140019	-1.051079	-2.813377
36	6	0	-0.062274	-1.904209	-1.962706
37	6	0	-2.868431	-1.894464	-1.964006
38	1	0	-2.665094	-0.406870	-3.512261
39	6	0	-0.751634	-2.701171	-1.033887
40	6	0	-2.147711	-2.682509	-1.053961
41	1	0	-2.683658	-3.281190	-0.323971
42	6	0	0.000000	-3.531862	0.000000
43	1	0	-0.723386	-4.189287	0.494778
44	1	0	0.723386	-4.189287	-0.494778
45	6	0	-4.354167	1.945942	2.023644
46	6	0	-5.031355	3.126000	1.703701
47	6	0	-5.093574	0.823836	2.438677
48	6	0	-6.431737	3.199382	1.808205
49	1	0	-4.494995	4.013895	1.397538
50	6	0	-6.490539	0.892424	2.555875
51	1	0	-4.563341	-0.088922	2.660301
52	6	0	-7.158975	2.089107	2.241980
53	6	0	-4.354167	-1.945942	-2.023644
54	6	0	-5.031355	-3.126000	-1.703701
55	6	0	-5.093574	-0.823836	-2.438677
56	6	0	-6.431737	-3.199382	-1.808205
57	1	0	-4.494995	-4.013895	-1.397538
58	6	0	-6.490539	-0.892424	-2.555875
59	1	0	-4.563341	0.088922	-2.660301
60	6	0	-7.158975	-2.089107	-2.241980
61	6	0	4.354167	1.945942	-2.023644
62	6	0	5.093574	0.823836	-2.438677
63	6	0	5.031355	3.126000	-1.703701
64	6	0	6.431737	3.199382	-1.808205
65	1	0	4.563341	-0.088922	-2.660301
66	6	0	6.490539	0.892424	-2.555875
67	1	0	4.494995	4.013895	-1.397538
68	6	0	7.158975	2.089107	-2.241980

69	6	0	4.354167	-1.945942	2.023644
70	6	0	5.031355	-3.126000	1.703701
71	6	0	5.093574	-0.823836	2.438677
72	6	0	6.431737	-3.199382	1.808205
73	1	0	4.494995	-4.013895	1.397538
74	6	0	6.490539	-0.892424	2.555875
75	1	0	4.563341	0.088922	2.660301
76	6	0	7.158975	-2.089107	2.241980
77	6	0	1.819716	-2.924104	-2.937393
78	1	0	1.515411	-2.689604	-3.966520
79	1	0	2.909848	-2.892318	-2.865457
80	1	0	1.471825	-3.937426	-2.696668
81	6	0	1.819716	2.924104	2.937393
82	1	0	1.515411	2.689604	3.966520
83	1	0	2.909848	2.892318	2.865457
84	1	0	1.471825	3.937426	2.696668
85	8	0	1.322124	1.961897	2.009408
86	8	0	1.322124	-1.961897	-2.009408
87	6	0	-1.819716	2.924104	-2.937393
88	1	0	-1.515411	2.689604	-3.966520
89	1	0	-2.909848	2.892318	-2.865457
90	1	0	-1.471825	3.937426	-2.696668
91	6	0	-1.819716	-2.924104	2.937393
92	1	0	-1.515411	-2.689604	3.966520
93	1	0	-2.909848	-2.892318	2.865457
94	1	0	-1.471825	-3.937426	2.696668
95	8	0	-1.322124	-1.961897	2.009408
96	8	0	-1.322124	1.961897	-2.009408
97	1	0	-8.234169	-2.087247	-2.313221
98	1	0	-8.234169	2.087247	2.313221
99	1	0	8.234169	2.087247	-2.313221
100	1	0	8.234169	-2.087247	2.313221
101	7	0	7.047966	-4.414752	1.407024
102	7	0	7.306130	0.185260	2.995440
103	7	0	7.306130	-0.185260	-2.995440
104	7	0	7.047966	4.414752	-1.407024
105	7	0	-7.306130	0.185260	-2.995440
106	7	0	-7.047966	-4.414752	-1.407024
107	7	0	-7.047966	4.414752	1.407024
108	7	0	-7.306130	-0.185260	2.995440
109	8	0	6.419736	-5.126235	0.539142
110	8	0	8.498092	-0.104866	3.376224
111	8	0	6.419736	5.126235	-0.539142
112	8	0	8.498092	0.104866	-3.376224
113	8	0	-6.419736	-5.126235	-0.539142
114	8	0	-8.498092	-0.104866	-3.376224
115	8	0	-6.419736	5.126235	0.539142
116	8	0	-8.498092	0.104866	3.376224
117	6	0	8.365955	-4.952626	1.922138
118	6	0	8.365955	4.952626	-1.922138
119	6	0	6.921198	-1.653982	-2.990004
120	6	0	6.921198	1.653982	2.990004
121	6	0	-8.365955	-4.952626	-1.922138
122	6	0	-6.921198	-1.653982	2.990004
123	6	0	-8.365955	4.952626	1.922138
124	6	0	-6.921198	1.653982	-2.990004
125	6	0	9.522587	-4.314730	1.125891
126	1	0	9.369614	-4.469098	0.052775
127	1	0	9.620297	-3.241339	1.308120
128	1	0	10.469530	-4.787845	1.408736
129	6	0	9.522587	4.314730	-1.125891
130	1	0	9.369614	4.469098	-0.052775
131	1	0	9.620297	3.241339	-1.308120
132	1	0	10.469530	4.787845	-1.408736
133	6	0	6.295458	2.038513	1.636935
134	1	0	6.192618	3.126872	1.573341
135	1	0	6.945212	1.723541	0.814645
136	1	0	5.309956	1.602467	1.465766
137	6	0	6.295458	-2.038513	-1.636935
138	1	0	6.192618	-3.126872	-1.573341
139	1	0	6.945212	-1.723541	-0.814645
140	1	0	5.309956	-1.602467	-1.465766
141	6	0	-9.522587	4.314730	1.125891
142	1	0	-9.369614	4.469098	0.052775
143	1	0	-9.620297	3.241339	1.308120
144	1	0	-10.469530	4.787845	1.408736
145	6	0	-6.295458	-2.038513	1.636935
146	1	0	-6.192618	-3.126872	1.573341
147	1	0	-6.945212	-1.723541	0.814645
148	1	0	-5.309956	-1.602467	1.465766
149	6	0	-9.522587	-4.314730	-1.125891
150	1	0	-9.369614	-4.469098	-0.052775
151	1	0	-9.620297	-3.241339	-1.308120
152	1	0	-10.469530	-4.787845	-1.408736
153	6	0	-6.295458	2.038513	-1.636935
154	1	0	-6.192618	3.126872	-1.573341
155	1	0	-6.945212	1.723541	-0.814645
156	1	0	-5.309956	1.602467	-1.465766
157	6	0	8.215714	2.462665	3.173464
158	1	0	8.924977	2.262615	2.365962
159	1	0	7.957919	3.526807	3.156769
160	1	0	8.707963	2.231073	4.119189
161	6	0	8.361140	6.470374	-1.672359

```
  162          1             0        9.292573    6.889913   -2.066934
  163          1             0        7.520220    6.950915   -2.180953
  164          1             0        8.290468    6.703407   -0.609329
  165          6             0        8.361140   -6.470374    1.672359
  166          1             0        9.292573   -6.889913    2.066934
  167          1             0        7.520220   -6.950915    2.180953
  168          1             0        8.290468   -6.703407    0.609329
  169          6             0        8.215714   -2.462665   -3.173464
  170          1             0        8.924977   -2.262615   -2.365962
  171          1             0        7.957919   -3.526807   -3.156769
  172          1             0        8.707963   -2.231073   -4.119189
  173          6             0       -8.361140    6.470374    1.672359
  174          1             0       -9.292573    6.889913    2.066934
  175          1             0       -7.520220    6.950915    2.180953
  176          1             0       -8.290468    6.703407    0.609329
  177          6             0       -8.215714   -2.462665    3.173464
  178          1             0       -8.924977   -2.262615    2.365962
  179          1             0       -7.957919   -3.526807    3.156769
  180          1             0       -8.707963   -2.231073    4.119189
  181          6             0       -8.215714    2.462665   -3.173464
  182          1             0       -8.924977    2.262615   -2.365962
  183          1             0       -7.957919    3.526807   -3.156769
  184          1             0       -8.707963    2.231073   -4.119189
  185          6             0       -8.361140   -6.470374   -1.672359
  186          1             0       -9.292573   -6.889913   -2.066934
  187          1             0       -7.520220   -6.950915   -2.180953
  188          1             0       -8.290468   -6.703407   -0.609329
  189          6             0       -5.986817   -1.944875    4.181498
  190          1             0       -6.469947   -1.656495    5.120935
  191          1             0       -5.773608   -3.018977    4.222786
  192          1             0       -5.032354   -1.416668    4.116104
  193          6             0       -8.500131   -4.705876   -3.436137
  194          1             0       -8.574496   -3.650756   -3.703468
  195          1             0       -7.646920   -5.135236   -3.972175
  196          1             0       -9.407981   -5.203173   -3.793967
  197          6             0       -5.986817    1.944875   -4.181498
  198          1             0       -6.469947    1.656495   -5.120935
  199          1             0       -5.773608    3.018977   -4.222786
  200          1             0       -5.032354    1.416668   -4.116104
  201          6             0       -8.500131    4.705876    3.436137
  202          1             0       -8.574496    3.650756    3.703468
  203          1             0       -7.646920    5.135236    3.972175
  204          1             0       -9.407981    5.203173    3.793967
  205          6             0        5.986817   -1.944875   -4.181498
  206          1             0        6.469947   -1.656495   -5.120935
  207          1             0        5.773608   -3.018977   -4.222786
  208          1             0        5.032354   -1.416668   -4.116104
  209          6             0        8.500131   -4.705876    3.436137
  210          1             0        8.574496   -3.650756    3.703468
  211          1             0        7.646920   -5.135236    3.972175
  212          1             0        9.407981   -5.203173    3.793967
  213          6             0        8.500131    4.705876   -3.436137
  214          1             0        8.574496    3.650756   -3.703468
  215          1             0        7.646920    5.135236   -3.972175
  216          1             0        9.407981    5.203173   -3.793967
  217          6             0        5.986817    1.944875    4.181498
  218          1             0        6.469947    1.656495    5.120935
  219          1             0        5.773608    3.018977    4.222786
  220          1             0        5.032354    1.416668    4.116104
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      0.0224500      0.0082013      0.0075689
 Standard basis: 6-31G(d) (6D, 7F)
SCF Done:  E(UB+HF-LYP) =  -4760.98909877     A.U. after    8 cycles
            Convg  =    0.3127D-08             -V/T =  2.0095
            S**2   =  20.1142
 Annihilation of the first spin contaminant:
 S**2 before annihilation    20.1142,   after    20.0030
The electronic state is 9-A
    Item               Value     Threshold  Converged?
 Maximum Force            0.000004     0.000450     YES
 RMS     Force            0.000001     0.000300     YES
 Maximum Displacement     0.001512     0.001800     YES
 RMS     Displacement     0.000288     0.001200     YES
 Predicted change in Energy=-9.172121D-09
 Optimization completed.
    -- Stationary point found.
```

Nitroxide octaradical 3a (^{9}A state) at the UB3LYP/6-31G(d,p) level (gas phase).

```
Stoichiometry    C88H112N8O12(9)
 Framework group  D2[C2(C.C),C2'(C.C),X(C84H112N8O12)]
 Deg. of freedom   164
 Full point group                 D2      NOp   4
 Largest Abelian subgroup         D2      NOp   4
 Largest concise Abelian subgroup D2      NOp   4
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -2.140704    1.048693    2.810432
```

2	6	0	-0.746176	1.018621	2.810858
3	6	0	-0.063217	1.904156	1.961813
4	6	0	-0.752420	2.700863	1.032717
5	6	0	-2.148414	2.681150	1.051528
6	6	0	-2.868556	1.892177	1.960958
7	1	0	-2.665832	0.404279	3.508204
8	1	0	-2.684227	3.279640	0.322139
9	6	0	0.000000	0.000000	3.661759
10	1	0	0.725323	0.493322	4.317073
11	1	0	-0.725323	-0.493322	4.317073
12	6	0	0.000000	3.531488	0.000000
13	1	0	0.722385	4.187935	0.495512
14	1	0	-0.722385	4.187935	-0.495512
15	6	0	0.746176	-1.018621	2.810858
16	6	0	2.140704	-1.048693	2.810432
17	6	0	0.063217	-1.904156	1.961813
18	6	0	2.868556	-1.892177	1.960958
19	1	0	2.665832	-0.404279	3.508204
20	6	0	0.752420	-2.700863	1.032717
21	6	0	2.148414	-2.681150	1.051528
22	1	0	2.684227	-3.279640	0.322139
23	6	0	0.752420	2.700863	-1.032717
24	6	0	2.148414	2.681150	-1.051528
25	6	0	0.063217	1.904156	-1.961813
26	6	0	2.868556	1.892177	-1.960958
27	1	0	2.684227	3.279640	-0.322139
28	6	0	0.746176	1.018621	-2.810858
29	6	0	2.140704	1.048693	-2.810432
30	1	0	2.665832	0.404279	-3.508204
31	6	0	0.000000	0.000000	-3.661759
32	1	0	-0.725323	0.493322	-4.317073
33	1	0	0.725323	-0.493322	-4.317073
34	6	0	-0.746176	-1.018621	-2.810858
35	6	0	-2.140704	-1.048693	-2.810432
36	6	0	-0.063217	-1.904156	-1.961813
37	6	0	-2.868556	-1.892177	-1.960958
38	1	0	-2.665832	-0.404279	-3.508204
39	6	0	-0.752420	-2.700863	-1.032717
40	6	0	-2.148414	-2.681150	-1.051528
41	1	0	-2.684227	-3.279640	-0.322139
42	6	0	0.000000	-3.531488	0.000000
43	1	0	-0.722385	-4.187935	0.495512
44	1	0	0.722385	-4.187935	-0.495512
45	6	0	-4.354225	1.942860	2.020375
46	6	0	-5.030514	3.125067	1.707442
47	6	0	-5.092908	0.817903	2.428589
48	6	0	-6.430984	3.197644	1.811887
49	1	0	-4.495257	4.014782	1.406330
50	6	0	-6.489896	0.886816	2.546784
51	1	0	-4.562605	-0.095983	2.643048
52	6	0	-7.158539	2.084951	2.239197
53	6	0	-4.354225	-1.942860	-2.020375
54	6	0	-5.030514	-3.125067	-1.707442
55	6	0	-5.092908	-0.817903	-2.428589
56	6	0	-6.430984	-3.197644	-1.811887
57	1	0	-4.495257	-4.014782	-1.406330
58	6	0	-6.489896	-0.886816	-2.546784
59	1	0	-4.562605	0.095983	-2.643048
60	6	0	-7.158539	-2.084951	-2.239197
61	6	0	4.354225	1.942860	-2.020375
62	6	0	5.092908	0.817903	-2.428589
63	6	0	5.030514	3.125067	-1.707442
64	6	0	6.430984	3.197644	-1.811887
65	1	0	4.562605	-0.095983	-2.643048
66	6	0	6.489896	0.886816	-2.546784
67	1	0	4.495257	4.014782	-1.406330
68	6	0	7.158539	2.084951	-2.239197
69	6	0	4.354225	-1.942860	2.020375
70	6	0	5.030514	-3.125067	1.707442
71	6	0	5.092908	-0.817903	2.428589
72	6	0	6.430984	-3.197644	1.811887
73	1	0	4.495257	-4.014782	1.406330
74	6	0	6.489896	-0.886816	2.546784
75	1	0	4.562605	0.095983	2.643048
76	6	0	7.158539	-2.084951	2.239197
77	6	0	1.817930	-2.925470	-2.938079
78	1	0	1.514845	-2.691416	-3.967016
79	1	0	2.907554	-2.897178	-2.867630
80	1	0	1.469147	-3.938334	-2.699499
81	6	0	1.817930	2.925470	2.938079
82	1	0	1.514845	2.691416	3.967016
83	1	0	2.907554	2.897178	2.867630
84	1	0	1.469147	3.938334	2.699499
85	8	0	1.321180	1.962798	2.009324
86	8	0	1.321180	-1.962798	-2.009324
87	6	0	-1.817930	2.925470	-2.938079
88	1	0	-1.514845	2.691416	-3.967016
89	1	0	-2.907554	2.897178	-2.867630
90	1	0	-1.469147	3.938334	-2.699499
91	6	0	-1.817930	-2.925470	2.938079
92	1	0	-1.514845	-2.691416	3.967016
93	1	0	-2.907554	-2.897178	2.867630
94	1	0	-1.469147	-3.938334	2.699499

95	8	0	-1.321180	-1.962798	2.009324
96	8	0	-1.321180	1.962798	-2.009324
97	1	0	-8.233062	-2.081240	-2.312957
98	1	0	-8.233062	2.081240	2.312957
99	1	0	8.233062	2.081240	-2.312957
100	1	0	8.233062	-2.081240	2.312957
101	7	0	7.046094	-4.416044	1.419733
102	7	0	7.305891	0.192858	2.980062
103	7	0	7.305891	-0.192858	-2.980062
104	7	0	7.046094	4.416044	-1.419733
105	7	0	-7.305891	0.192858	-2.980062
106	7	0	-7.046094	-4.416044	-1.419733
107	7	0	-7.046094	4.416044	1.419733
108	7	0	-7.305891	-0.192858	2.980062
109	8	0	6.408765	-5.142749	0.571582
110	8	0	8.503394	-0.092396	3.346513
111	8	0	6.408765	5.142749	-0.571582
112	8	0	8.503394	0.092396	-3.346513
113	8	0	-6.408765	-5.142749	-0.571582
114	8	0	-8.503394	-0.092396	-3.346513
115	8	0	-6.408765	5.142749	0.571582
116	8	0	-8.503394	0.092396	3.346513
117	6	0	8.376073	-4.939297	1.920899
118	6	0	8.376073	4.939297	-1.920899
119	6	0	6.913093	-1.659962	-2.985872
120	6	0	6.913093	1.659962	2.985872
121	6	0	-8.376073	-4.939297	-1.920899
122	6	0	-6.913093	-1.659962	2.985872
123	6	0	-8.376073	4.939297	1.920899
124	6	0	-6.913093	1.659962	-2.985872
125	6	0	9.516215	-4.292058	1.109016
126	1	0	9.353601	-4.454193	0.039606
127	1	0	9.603574	-3.217764	1.283938
128	1	0	10.470470	-4.752306	1.383972
129	6	0	9.516215	4.292058	-1.109016
130	1	0	9.353601	4.454193	-0.039606
131	1	0	9.603574	3.217764	-1.283938
132	1	0	10.470470	4.752306	-1.383972
133	6	0	6.287197	2.050723	1.634904
134	1	0	6.176642	3.137769	1.580319
135	1	0	6.940542	1.747559	0.812505
136	1	0	5.306475	1.608855	1.458243
137	6	0	6.287197	-2.050723	-1.634904
138	1	0	6.176642	-3.137769	-1.580319
139	1	0	6.940542	-1.747559	-0.812505
140	1	0	5.306475	-1.608855	-1.458243
141	6	0	-9.516215	4.292058	1.109016
142	1	0	-9.353601	4.454193	0.039606
143	1	0	-9.603574	3.217764	1.283938
144	1	0	-10.470470	4.752306	1.383972
145	6	0	-6.287197	-2.050723	1.634904
146	1	0	-6.176642	-3.137769	1.580319
147	1	0	-6.940542	-1.747559	0.812505
148	1	0	-5.306475	-1.608855	1.458243
149	6	0	-9.516215	-4.292058	-1.109016
150	1	0	-9.353601	-4.454193	-0.039606
151	1	0	-9.603574	-3.217764	-1.283938
152	1	0	-10.470470	-4.752306	-1.383972
153	6	0	-6.287197	2.050723	-1.634904
154	1	0	-6.176642	3.137769	-1.580319
155	1	0	-6.940542	1.747559	-0.812505
156	1	0	-5.306475	1.608855	-1.458243
157	6	0	8.203090	2.472930	3.177734
158	1	0	8.912693	2.284477	2.369235
159	1	0	7.940087	3.534766	3.172672
160	1	0	8.695929	2.232331	4.119811
161	6	0	8.382918	6.457140	-1.674997
162	1	0	9.323857	6.865493	-2.055364
163	1	0	7.555630	6.944242	-2.197148
164	1	0	8.296750	6.692371	-0.614587
165	6	0	8.382918	-6.457140	1.674997
166	1	0	9.323857	-6.865493	2.055364
167	1	0	7.555630	-6.944242	2.197148
168	1	0	8.296750	-6.692371	0.614587
169	6	0	8.203090	-2.472930	-3.177734
170	1	0	8.912693	-2.284477	-2.369235
171	1	0	7.940087	-3.534766	-3.172672
172	1	0	8.695929	-2.232331	-4.119811
173	6	0	-8.382918	6.457140	1.674997
174	1	0	-9.323857	6.865493	2.055364
175	1	0	-7.555630	6.944242	2.197148
176	1	0	-8.296750	6.692371	0.614587
177	6	0	-8.203090	-2.472930	3.177734
178	1	0	-8.912693	-2.284477	2.369235
179	1	0	-7.940087	-3.534766	3.172672
180	1	0	-8.695929	-2.232331	4.119811
181	6	0	-8.203090	2.472930	-3.177734
182	1	0	-8.912693	2.284477	-2.369235
183	1	0	-7.940087	3.534766	-3.172672
184	1	0	-8.695929	2.232331	-4.119811
185	6	0	-8.382918	-6.457140	-1.674997
186	1	0	-9.323857	-6.865493	-2.055364
187	1	0	-7.555630	-6.944242	-2.197148

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    188          1           0       -8.296750   -6.692371   -0.614587
    189          6           0       -5.975585   -1.936197    4.178067
    190          1           0       -6.459312   -1.644992    5.115039
    191          1           0       -5.755790   -3.007535    4.226336
    192          1           0       -5.025691   -1.402787    4.108399
    193          6           0       -8.525178   -4.686650   -3.432323
    194          1           0       -8.590994   -3.631081   -3.695710
    195          1           0       -7.683910   -5.123696   -3.978636
    196          1           0       -9.441580   -5.172705   -3.780289
    197          6           0       -5.975585    1.936197   -4.178067
    198          1           0       -6.459312    1.644992   -5.115039
    199          1           0       -5.755790    3.007535   -4.226336
    200          1           0       -5.025691    1.402787   -4.108399
    201          6           0       -8.525178    4.686650    3.432323
    202          1           0       -8.590994    3.631081    3.695710
    203          1           0       -7.683910    5.123696    3.978636
    204          1           0       -9.441580    5.172705    3.780289
    205          6           0        5.975585   -1.936197   -4.178067
    206          1           0        6.459312   -1.644992   -5.115039
    207          1           0        5.755790   -3.007535   -4.226336
    208          1           0        5.025691   -1.402787   -4.108399
    209          6           0        8.525178   -4.686650    3.432323
    210          1           0        8.590994   -3.631081    3.695710
    211          1           0        7.683910   -5.123696    3.978636
    212          1           0        9.441580   -5.172705    3.780289
    213          6           0        8.525178    4.686650   -3.432323
    214          1           0        8.590994    3.631081   -3.695710
    215          1           0        7.683910    5.123696   -3.978636
    216          1           0        9.441580    5.172705   -3.780289
    217          6           0        5.975585    1.936197    4.178067
    218          1           0        6.459312    1.644992    5.115039
    219          1           0        5.755790    3.007535    4.226336
    220          1           0        5.025691    1.402787    4.108399
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      0.0225035      0.0082036      0.0075710
 Standard basis: 6-31G(d,p) (6D, 7F)
SCF Done:  E(UB3LYP) =  -4761.14951755     A.U. after    9 cycles
             Convg  =    0.3337D-08             -V/T =  2.0095
 <Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 4.0000 <S**2>=20.1152 S= 4.0128
 <L.S>= 0.000000000000E+00
 Annihilation of the first spin contaminant:
 S**2 before annihilation    20.1152,   after    20.0031
The electronic state is 9-A
Item               Value     Threshold  Converged?
 Maximum Force            0.000002     0.000450     YES
 RMS     Force            0.000000     0.000300     YES
 Maximum Displacement     0.001100     0.001800     YES
 RMS     Displacement     0.000157     0.001200     YES
 Predicted change in Energy=-6.788989D-10
 Optimization completed.
    -- Stationary point found.
```